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CERTIFICATION REPORT

The Certification of the Mass Fractions of As, Br, Cd, Cl, Cr, Hg, Pb, S, Sb, Sn and Zn in Low-Density Polyethylene: ERM®-EC681m

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Abstract
This report describes the production of ERM-EC681m, a low-density polyethylene material certified for the mass fraction of elements. The material was produced following ISO Guide 34:2009.
An LDPE material containing certain elements was prepared from commercially sourced low-density polyethylene and organic and inorganic pigments. The material was extruded, mixed and filled into bottles.
Between-bottle homogeneity was quantified and stability during dispatch and storage were assessed following ISO Guide 35:2006. The within-unit homogeneity was quantified to determine the minimum sample intake.
The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, instability and characterisation.
The material is intended for the quality control and/or assessment of method performance. As any reference material, it can also be used for control charts, validation studies or calibration of methods. The CRM is available in glass bottles containing 100 g of polyethylene granulate. The minimum amount of sample to be used is 150 mg for the determination of Cl and 60 mg for the determination of all other elements.
The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

CERTIFICATION REPORT

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Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM-EC681m, a low-density polyethylene material certified for the mass fraction of elements. The material was produced following ISO Guide 34:2009 [1].

An LDPE material containing certain elements was prepared from commercially sourced low-density polyethylene and organic and inorganic pigments. The material was extruded, mixed and filled into bottles.

Between-bottle homogeneity was quantified and stability during dispatch and storage were assessed following ISO Guide 35:2006 [2]. The within-unit homogeneity was quantified to determine the minimum sample intake.

The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and include uncertainties related to possible inhomogeneity, instability and characterisation.

The material is intended for the quality control and/or assessment of method performance. As any reference material, it can also be used for control charts, validation studies or calibration of methods. The CRM is available in glass bottles containing 100 g of polyethylene granulate. The minimum amount of sample to be used is 150 mg for the determination of Cl and 60 mg for the determination of all other elements.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following certified values were assigned:

	Mass fraction		
	Certified value[1]	Uncertainty [2)]	Unit
As	17.0	1.2	mg/kg
Br	1.43	0.08	g/kg
Cd	146	5	mg/kg
Cl	0.38	0.06	g/kg
Cr	45.1	1.9	mg/kg
Hg	9.9	0.8	mg/kg
Pb	69.7	2.5	mg/kg
S	0.64	0.10	g/kg
Sb	86	7	mg/kg
Sn	99	6	mg/kg
Zn	1.17	0.04	g/kg

1) Certified values are values that fulfil the highest standards of accuracy. The given value(s) represent(s) the unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of units (SI).

2) The uncertainty is the expanded uncertainty of the certified value with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

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Glossary

AES	Atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CI	Confidence interval
CRM	Certified reference material
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
DMA	Direct mercury analyser
EC	European Commission
EDXRF	Energy-dispersive x-ray spectrometry
ERM®	Trademark of European Reference Materials
EU	European Union
ETAAS	Electrothermal atomic absorption spectrometry
GUM	Guide to the Expression of Uncertainty in Measurements [3]
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-QMS	ICP-Quadrupole mass spectrometry
ICP-SFMS	ICP-Sector field mass spectrometry
ID	Isotope dilution
IR	Infrared
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0NAA	k_0-Neutron activation analysis
k_2'	Factor for the two-sided 95 % tolerance limits for a normal distribution
LDPE	Low-density polyethylene
LOD	Limit of detection
$\overline{m}$	Average mass used during the minimum-sample intake measurements
m_{min}	Minimum sample mass representative for the whole bottle
$MS_{between}$	Mean of squares between-bottle from an ANOVA
MS_{within}	Mean of squares within-bottle from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
NIST	US National Institute of Standards and Technology
rel	Index denoting relative figures (uncertainties etc.)
QCM	Quality control material
RM	Reference material
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added if appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added if appropriate
se	Standard error
SI	International System of Units
$s_{m,rel}$	Relative standard deviation obtained in the minimum sample intake study

s_{wb}	Within-unit standard deviation; an additional index "rel" is added if appropriate
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added if appropriate
T	Temperature
t	Time
t_i	Time point for each replicate
t_{sl}	Proposed shelf life
u	Standard uncertainty
U	Expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added if appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added if appropriate
u_{char}	Standard uncertainty related to the material characterisation; an additional index "rel" is added if appropriate
u_{CRM}	Combined standard uncertainty related to the certified value; an additional index "rel" is added if appropriate
U_{CRM}	Expanded uncertainty related to the certified value; an additional index "rel" is added if appropriate
u_{lts}	Standard uncertainty related to the long-term stability; an additional index "rel" is added if appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added if appropriate
u_t	Standard uncertainty of trueness
$u_{target,rel}$	Maximum relative uncertainty acceptable for sub sampling
UV	Ultraviolet
$\overline{x}$	Arithmetic mean
$\overline{x}_{ns}$	Arithmetic mean of all results of normal stock samples
$\overline{x}_{ref}$	Arithmetic mean of results of reference samples
α	Significance level
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

Protection of the environment and human health from excessive heavy metal loads is an important goal for regulators. To achieve this, the European Union has passed legislation to limit the load of certain elements in various products, amongst them Directive 94/62/EC (packaging directive) [4], Directive 2011/65/EU (restriction of the use of certain hazardous substances in electric and electronic equipment) [5] and Directive 2000/53/EC (end of live vehicles) [6].

- Directive 94/62/EC concerns plastics packaging and packaging material and regulates the amounts of Cd, Cr, Hg and Pb in plastics used for packaging. Article 11 of this Directive states that the sum of Pb, Cd, Hg and Cr(VI) must be below 100 mg/kg as of June 30, 2001.
- Directive 2011/65/EU ("RoHS 2") aims at reducing the amount of hazardous substances in electric and electronic equipment. Use of Pb, Hg, Cr(VI), Cd and polybrominated flame retardants is prohibited unless no alternatives exist for certain applications. In addition to the sum, maximum limits for Pb, Hg and Cr (VI) (1 g/kg) and Cd (100 mg/kg) in homogeneous materials are set. This directive also sets upper limits for the mass fractions of of polybrominated flame retardants. Measurement of total Br is often used as screening for these compounds. Legislation similar to 2011/65/EU exist, amongst others, in the People's Republic of China, Japan, the Republic of Korea, Turkey and some states of the USA (e.g. California).
- Similarly, Directive 2000/53/EC aims at reducing the amount of hazardous substances entering the environment from old vehicles. As in Directive 2011/65/EU, Council Decision 2005/673/EC [7] sets maximum limits of 1 g/kg in homogeneous materials for Pb, Hg, Cr(VI) and 0.1 g/kg for Cd.
- Cl, S, Sb and Sn are not regulated, but as they are volatile elements and CRMs for these elements are scarce, certification is desirable as well. This assessment was confirmed in a survey of users of BCR-680 and BCR-681.

In support of these directives, several certified reference materials (CRMs) have been produced by the European Commission, namely a set of four polyethylene materials (on behalf of the German Verband der Automobilindustrie e.V., Frankfurt) [8] and two additional high-density polyethylene materials, BCR-680 and BCR-681 [9]. BCR-680 and BCR-681 were re-branded as ERM-EC680 and ERM-EC681 in 2004. These materials were exhausted in 2006 and two replacement batches (ERM-EC680k and ERM-EC681k) consisting of low-density polyethylene (LDPE) were released in 2007. This report describes the production of ERM-EC681m, the replacement batch of ERM-EC681k.

1.2 Choice of the material

As the new material should be a close replacement of the previous one, it was decided to use again LDPE as matrix with similar element levels as the previous batch, ERM-EC681k. As for the pigments used, some changes were introduced: ERM-EC681k contained Cr_2O_3 and SnO_2, which are virtually not digestible by acid digestion methods, so they were replaced by pigments also accessible for wet-chemistry methods. In addition, pigments were also selected according to commercial availability. Therefore, $PbCrCrO_4/PbSO_4$ was replaced by Pb_3O_4 and $CaCrO_4$

1.3 Design of the project

The goal was to produce a CRM similar to ERM-EC681k.

After the processing, homogeneity was assessed via an experimental homogeneity study. The stability of the material was based on information on the stability of the matrix and pigments, the stability of the previous batches and a limited stability study of the material itself.

The characterisation was based on an intercomparison involving expert laboratories with demonstrated competence in the determination of trace elements. Care was taken to select combinations of different sample preparation/quantification techniques to demonstrate the absence of a significant method bias.

The data of the characterisation study were subjected to a technical and statistical evaluation and certified values were assigned.

2 Participants

2.1 Project management and data evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

AIMPLAS-Instituto Tecnológico del Plástico, Valencia, Spain

2.3 Homogeneity study

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

Technische Universität Bergakademie Freiberg, Freiberg, Germany

2.4 Stability study

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

2.5 Characterisation

ALS Scandinavia AB, Luleå, Sweden
(measurements for one method under the scope of ISO/IEC 17025 accreditation SWEDAC 2030)

Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

Bundesanstalt für Materialforschung und Prüfung, Berlin, Germany
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ECN, Petten, The Netherlands

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

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Università Degli Studi di Ferrara, Ferrara, Italy

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium

3 Material processing and process control

3.1 Origin and purity of the starting material

The material was prepared from general purpose grade LDPE and the inorganic pigments shown in Table 1.

Table 1: Pigments used for the production of ERM-EC681m. Purity values given are as specified by the supplier of the pigments.

Compound	Pigment name	Purity [%]	Comment
As_2O_3	Arsenic trioxide	>99	Same as used in the production of ERM-EC681k
$C_{32}Br_6Cl_{10}CuN_8$	Pigment Green 36; Heliogen Green L9361	95	Same as used in the production of ERM-EC681k
$C_{32}Cl_{16}CuN_8$	Pigment Green 7; Heliogen Green L8735	95	Same as used in the production of ERM-EC681k
HgS	Pigment Red 106; Vermilion	99	Same as used in the production of ERM-EC681k
Sb_2O_3	Pigment White 11	98	Same as used in the production of ERM-EC681k
CdS	Pigment Yellow 37	98	A mixture of CdS/ZnS (Pigment Yellow 35) was used in the production of ERM-EC681k
ZnS	Pigment White 7; Sactolith HDS	98	
SnS_2	Pigment Yellow 38	98	Not used in the production of ERM-EC681k
Pb_3O_4	Pigment Red 105	96	Not used in the production of ERM-EC681k
$CaCrO_4$	Pigment Yellow 33	95	Not used in the production of ERM-EC681k

3.2 Processing

3.2.1 Processing of the plastic

A preliminary particle size determination showed that the median diameter (D_{50}) of all pigments was about 10 μm. During the production of BCR-681 it was found that particle sizes of 1 μm and below are required to ensure to ensure good repeatability even at low sample intakes [9]. Therefore, the pigments were dry-mixed in the appropriate portions for each

intermediate batch (see below) in a turbomixer and milled to a median particle size (D_{50}) of 1 µm.

An intermediate batch of high element mass fractions was prepared by mixing the milled pigments with pure LDPE (EXCEED LL6161RQ, Exxon Mobil Chemical) in a co-rotating twin screw extruder using a very-high shear screw design to ensure a good dispersion of the pigments. The obtained material was cooled in a water bath and cut into 3 x 3 mm pellets.

This intermediate product was diluted in a ratio 1:50 with pure LDPE (LLDPE M200024, Sabic), which does not contain any plasticisers. This dilution was performed a co-rotating twin screw extruder and gravimetric feeders to mix the fresh LDPE and the intermediate batch. The obtained material was cooled in a water bath and cut into 3 x 3 mm pellets.

Before preparation of the final batch, a test batch of 75 kg was prepared and samples were taken every 45 min (five samples in total). The samples were analysed for their trace element content by electron-dispersive x-ray spectrometry and were found homogeneous. The trace element distribution in the samples was investigated by scanning electron microscopy coupled with X-ray detection. These tests (Figure 1) showed the good dispersion of the pigments and the absence of agglomerates. These tests also confirmed the control of the preparation process and it was decided to proceed with the processing of the final batch. In total, 600 kg of the final batch were produced.

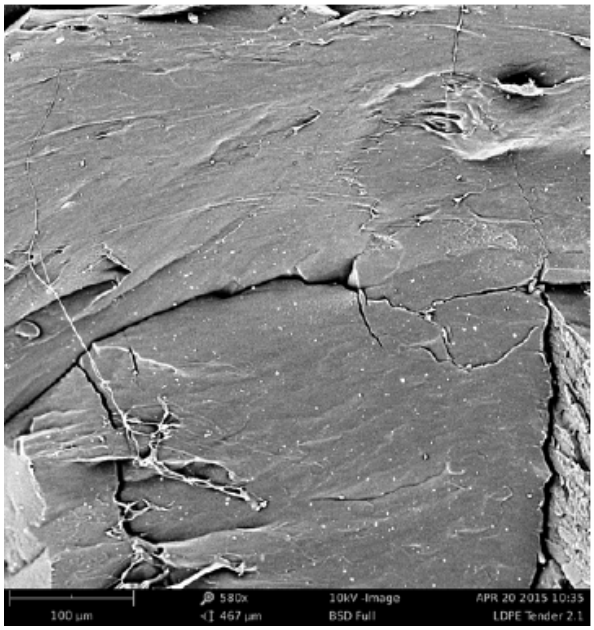

Figure 1: Representative scanning electron microscope image of ERM-EC681m. The white spots are the inorganic pigments; scale bar is 100 µm.

3.2.2 Mixing and bottling

The batch was split into two sub-batches of 300 kg and each sub-batch was mixed for 2 h in a three dimensional mixer. Each sub-batch was again split into two, one half of sub-batch 1 was combined with one half of sub-batch 2 and mixed again for 2 h. This process was repeated once. The mixing scheme for ERM-EC681m is given in Figure 2.

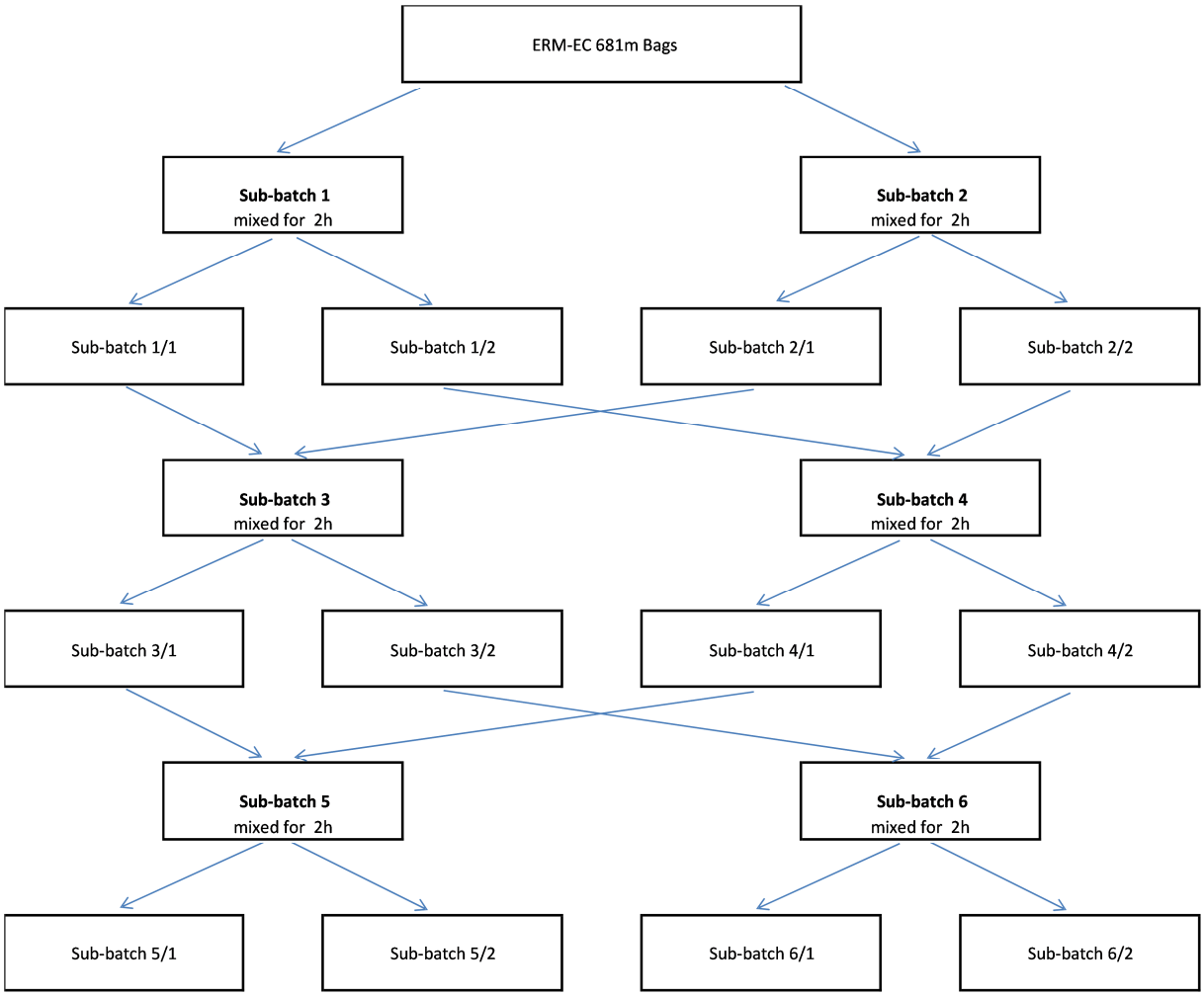

Figure 2: Mixing scheme of ERM-EC681m

The final material of each sub-batch was filled into amber brown bottles containing 100 g granulate each. The bottles were labelled in the filling sequence.

4 Homogeneity

A key requirement for any reference material is the equivalence between the material in the various bottles. In this respect, it is relevant whether the variation between bottles is significant compared to the uncertainty of the certified value. In contrast to that it is not relevant if this variation between bottles is significant compared to the analytical variation. Consequently, ISO Guide 34 requires RM producers to quantify the between bottle variation. This aspect is covered in between-bottle homogeneity studies.

The within-bottle inhomogeneity determines the minimum size of an aliquot that is representative for the whole bottle. As long as this minimum sample size is respected, within-bottle inhomogeneity does not influence the uncertainty of the certified values. Quantification of within-bottle inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-bottle homogeneity

The between-bottle homogeneity was evaluated to ensure that the certified values of the CRM are valid for all bottles of the material, within the stated uncertainty.

The number of selected bottles corresponds to approximately the cubic root of the total number of the produced bottles. 20 bottles were selected using a random stratified sampling scheme covering the whole batch for the between-bottle homogeneity test. For this, the batch was divided into 20 groups (with a similar number of bottles) and one bottle was selected randomly from each group. Three independent samples were taken from each selected bottle, and analysed by DMA for Hg (sample mass 20 mg) or EDXRF for all other elements (discs prepared from the granulate). The measurements were performed under repeatability conditions and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results are shown as graphs in Annex A.. Note that the results were obtained by one laboratory only. Although the absolute values of several elements differ from the certified values, this should not influence the homogeneity assessment, which compares only results within the measurement series.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence were detected on a 99 % significance level. None of the elements determined by EDXRF showed a trend in the analytical sequence, but for the data for Hg showed a significant trend on a 99 % confidence level, pointing at a signal drift in the analytical system. The correction of biases was found to combine the smallest uncertainty with the highest probability to cover the true value [10]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-bottle heterogeneities. As the analytical sequence and the bottle numbers were not correlated, the trend in the analytical sequence for Hg was corrected as shown below:

$$corrected\,result = measured\ \ result - b \cdot i \qquad \textbf{Equation 1}$$

b **=** slope of the linear regression

i **=** position of the result in the analytical sequence

All datasets (the trend-corrected dataset was used for Hg) were tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the bottle means. No outlying individual results or outlying bottle means were detected.

Quantification of between-bottle inhomogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-bottle variation (s_{bb}) from the within-bottle variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole bottle.

Evaluation by ANOVA requires bottle means which follow at least a unimodal distribution and results for each bottle that follow unimodal distributions with approximately the same standard deviations. Distribution of the bottle means was visually tested using histograms and normal probability plots. Too few data are available for each bottle to make a clear statement of the distribution of the individual data for each bottle. Therefore, it was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-bottle standard deviations. The results of all statistical evaluations are given in Table 2.

Table 2: Results of the statistical evaluation of the homogeneity studies Outliers were tested at a 99 % confidence level, trends were tested on a 95 % confidence level.

Element	Trends (anal. sequence before correction)		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Bottle means	Individual results	Bottle means
As	no	no	none	none	normal	normal
Br	no	no	none	none	normal	normal
Cd	no	no	none	none	normal	normal
Cl	no	no	none	none	normal	unimodal
Cr	no	no	none	none	normal	normal
Hg	yes	no	none	none	normal	normal
Pb	no	no	none	none	normal	normal
S	no	no	none	none	unimodal	unimodal
Sb	no	no	none	none	normal	unimodal
Sn	no	no	none	none	normal	normal
Zn	no	no	none	none	normal	normal

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-bottle variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [11]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–bottle standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \qquad \textbf{Equation 2}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \qquad \textbf{Equation 3}$$

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}} \qquad \textbf{Equation 4}$$

MS_{within} mean square within a bottle from an ANOVA

$MS_{between}$ mean squares between-bottle from an ANOVA

$\bar{y}$ mean of all results of the homogeneity study

n number of replicates per bottle

$v_{MSwithin}$ degrees of freedom of MS_{within}

The results of the evaluation of the between-bottle variation are summarised in

Table 3. The resulting values from the above equations were converted into relative uncertainties. In most cases, the uncertainty contribution for homogeneity was below 3 %. The only notable exceptions are Cl and S, where significant inhomogeneities were found.

Table 3: Results of the homogeneity study

Element	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
As	3.24	2.41	0.88	2.41
Br	1.79	0.18	0.49	0.49
Cd	2.56	1.12	0.70	1.12
Cl	12.59	6.77	3.44	6.77
Cr	3.18	1.49	0.87	1.49
Hg	7.85	n.c[1]	2.14	2.14
Pb	1.85	0.59	0.50	0.59
S	12.81	6.97	3.50	6.97
Sb	2.47	0.69	0.68	0.69
Sn	2.66	0.58	0.73	0.73
Zn	1.93	0.40	0.53	0.53

[1] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

The homogeneity study showed no outlying bottle means or trends in the filling sequence. Therefore the between-bottle standard deviation can be used as estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

4.2 Within-bottle homogeneity and minimum sample intake

The within-bottle homogeneity is closely correlated to the minimum sample intake. Individual aliquots of a material will not contain exactly the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole bottle and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

The minimum sample intake of the material was determined using solid sampling ICP-AES in the same way as has been described for solid sampling ETAAS [12] for As, Br, Cd, Cr, Hg, Pb, S, Sb, Sn and Zn.

Samples were cut using a ZrO_2 cutting tool and analysed on an ARCOS EOP ICP-spectrometer (SPECTRO A. I. GmbH & Co. KG, Kleve, Germany) in axial (EOP) observation of the ICP plasma equipped with a electrothermal vaporization unit (ETV 4050 A, Spectral Systems, Fürstenfeldbruck, Germany).

Sample intakes of about 0.30-0.47 mg were used. 17 individual pieces were measured and two subsamples were taken from each piece. The dataset for Cr contained one large outlier being a factor 10 higher than the other results. The dataset for Sb contained one outlier that was 50 % higher than the other results. The outlier for Cr might have been caused by the use of a stainless steel needle for picking up the samples and transferring them into the vaporisation unit, but no reason for the outlying Sb value could be found. As all pigments were milled together, any "nugget" would be expected to contain more than one pigment, causing high values for several elements, but this was not seen for the other elements in the same vaporisations.

Inclusion of the outliers would result in a minimum sample intake of 4500 mg to achieve a repeatability of 1.3 % for Cr and 80 mg to achieve a repeatability of 1.4 % for Sb. This high sample intake is contradicted by the results obtained by laboratory 5d, which obtained a relative standard deviation of 1.7 % for Cr on a sample intake of 150 g. Also the repeatabilities obtained from the other laboratories on similarly low sample intakes are low, showing that these outliers do not reflect reality. It was therefore concluded that the high values were due to some unidentified analytical artefact. These two values were removed from the evaluation.

The data was evaluated according to the following equation [13]:

$$m_{\min} = \left(\frac{k_2' \cdot s_{m,rel}}{u_{\text{target,rel}}} \right)^2 \cdot \overline{m} \qquad \textbf{Equation 5}$$

with $m_{\min}$ minimum sample mass, k'_2 factor for the two-sided 95 % tolerance limits for a normal distribution, $s_{m,\text{rel}}$ relative standard deviation of the homogeneity experiment, $u_{target,rel}$ maximum relative uncertainty acceptable for sub sampling and $\overline{m}$ the average mass used during the measurements (0.384 mg). Two times the uncertainty of characterisation ($u_{\text{char,rel}}$) as described in 6.4.2 was used as $u_{\text{target,rel}}$

The resulting minimum sample masses are summarised in Table 4.

Table 4: Minimum sample masses for the uncertainty of characterisation as determined by solid sampling ICP-AES

Element	$s_{\text{m,rel}}$ [%]	$u_{\text{char,rel}}$ [%]	$m_{\min}$ [mg]
As	5.7	1.4	9
Br	8.8	2.3	8
Cd	6.9	0.8	44
Cr	7.7	1.2	20
Hg	7.6	2.9	4
Pb	6.8	1.2	16
S	6.2	2.0	5
Sb	14.5	1.4	54
Sn	7.4	1.3	17
Zn	5.5	1.1	14

The overall minimum sample intake for this material, valid for all elements investigated, is set to 60 mg. No data are available for Cl due to the slight Cl contamination of the CF_4 used as modifier. The minimum sample intake for Cl is derived from the characterisation study: Several participants used sample intakes of 150 mg. The repeatability of the results (2-9 %) demonstrate the homogeneous distribution of Cl on that level.

5 Stability

Time, temperature and radiation were regarded as the most relevant influences on stability of the material. The influence of ultraviolet or visible radiation is minimised by the choice of the containment (amber glass bottles) which eliminates most of the incoming light. Also, materials are stored and dispatched in the dark, thus largely eliminating the possibility of degradation by radiation. Despite these precautions, stability of the samples against UV light was tested to assess any potential influence of radiation. This was also to assess the long-term stability of the material.

Stability assessment is necessary to establish conditions for storage (long-term stability) as well as for dispatch of the material to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature will be applied.

The short-term stability study was carried out using an isochronous design [14]. Following that approach, samples are stored for a particular time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the samples are analysed simultaneously under repeatability conditions which significantly improves the sensitivity of the stability tests.

5.1 Short-term stability study

For the short-term stability study, samples were stored at 60 °C for 0, 1, 2 and 4 weeks. The reference temperature was set to -20 °C. Five bottles per storage time were selected using a random stratified sampling scheme. From each bottle, three independent subsamples were measured by DMA (Hg) or EDXRF (all other elements). The measurements were performed under repeatability conditions and in a randomised sequence to be able to separate a potential analytical drift from a trend over storage time.

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. No outlying individual results were found, so all data were retained for statistical analysis and the estimation of u_{sts}.

Furthermore, the data were evaluated against storage time and regression lines of mass fraction versus time were calculated. The slopes of the regression lines were tested for statistical significance (loss/increase due to shipping conditions) and no significant trend was detected on a 99 % confidence level. The results of the measurements are shown in Annex B.

For testing the influence of UV irradiation, the granulate was placed in a single layer under an UV lamp (Sylvania G, 8W; distance from the lamp about 1 cm) and irradiated for 178 h. This intensive irradiation led to a slight colour change of the material (see Figure 3). Irradiated and non-irradiated samples were then analysed in one analytical run by digestion-ICP-AES. No significant difference between the element mass fractions in irradiated and non-irradiated samples was found (data not shown).). Also the temperature/pressure profile as measured by the microwave digestion system did not differ significantly between irradiated and non-irradiated samples, demonstrating also the structural stability of the polymer matrix against long-term exposure to UV radiation.

Figure 3: ERM-EC681m after 178 h of UV irradiation. Left: irradiated sample; right: non-irradiated sample

The fact that neither temperature nor UV irradiation influenced the element mass fractions demonstrates that the material can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability

Stability during storage was assessed using data from the two previous two batches of trace metals in plastic, based on the following considerations:

- Polyethylene is a very stable material. No plasticisers were added to prevent a change of mass by desorption of volatile compounds.
- Most pigments used are inorganic and are protected from environmental influences by the LDPE matrix and the amber glass bottle.
- All pigments (including the organic ones) used for ERM-EC681m, except SnS_2, Pb_3O_4, $CaCrO_4$, were also used in the production of ERM-EC680k and ERM-EC681k. This means that stability data on these previous batches give information on the stability of these pigments in a polyethylene matrix.
- Photo-oxidation of CdS to sulfates, carbonates and oxalates has been reported for paintings [15], but only over time scales of several decades.
- Pb_3O_4 is insoluble in water and alcohol, but soluble in hydrochloric and nitric acid and it also decomposes at temperatures above 500 °C. However, none of these conditions are expected in the storage of the CRMs. The stability of the pigment under normal storage conditions is shown by the still bright colours of medieval manuscripts that often used it [16].
  SnS_2 is also a pigment with long use: it has been used under the name "Mosaic gold" and its production is described as early as in the 15th century. Its use in several 14th and 15th century manuscripts demonstrates its stability under careful storage conditions [17]. The material is insoluble in water, but soluble in aqua regia and in alkaline solutions. It decomposes at 600 °C [18], showing its thermal stability.
  $CaCrO_4$ is soluble in water and acids, but is, like the other pigments, protected by the polyethylene matrix. It is a relatively recent pigment, which was first produced in the 19th

century [17]. It is used as pigment and as corrosion inhibitor.
This means that historical evidence is available for the stability of Pb_3O_4 and SnS_2. Based on its chemical properties, also $CaCrO_4$ should be stable, as long as the pigment itself is not brought into contact with water or reducing substances. As LDPE has a very low permeability to water, significant dissolution is virtually impossible and any actual effect will be picked up by the stability monitoring of the material conducted by IRMM.

- The first materials, ERM-EC680 and ERM-EC681 were produced in 1999. Stability tests in 2005 showed no degradation. The material was also used as quality control material in the certification of ERM-EC680k and ERM-EC681k and the mean of laboratory mean element mass fractions obtained on the materials at that time agreed with the certified values for all elements except Cr and Br at the low level, where differences of 4.4 % (Br) and 3.1 % (Cr), respectively, were observed.
- The follow-up batches ERM-EC680k and ERM-EC681k were produced in October 2006. Stability was confirmed by the stability monitoring performed in 2013, although there was disagreement between the two laboratories performing the test on the As mass fraction: one laboratory found a lower value, whereas the result of the other laboratory agreed with the certified value. Samples of this material were also used as quality control samples in the characterisation study of ERM-EC680m and ERM-EC681m and the mean of laboratory means agreed within the respective uncertainties except the mean value for As obtained during the characterisation study for ERM-EC681m. This confirms the stability of the material for all elements except As, which seems to change over time.

The data from the characterisation of ERM-EC681k, the stability test in 2013 and the combined result of the technically accepted data obtained (see section 6.4.1) during the characterisation study of ERM-EC681m are shown in Table 5. All data agreed with the certified values with the exception of the mean value for As obtained during the characterisation study for ERM-EC681m. A potential explanation for this effect could be the conversion of As_2O_3 to volatile AsH_3 by the hydrogen available in the polymer. Nevertheless, the stability data from the stability test in 2013 also confirm stability for As for at least 7 years.

Table 5: Certified values for ERM-EC681k and their standard uncertainty obtained in October 2006 (Sn and Zn are indicative values only), stability monitoring data and their uncertainties obtained in 2013 and mean of laboratory means and its standard error obtained in the characterisation study of ERM-EC681m in September 2015. For Cr and Sn (2015 data), only the data from k_0NAA were used, as ERM-EC681k contains pigments that are only partially acid-digestible.

Element	Characterisation study 2006: certified value ± u	Stability monitoring: average ± s (n=6)	Characterisation study 2015: average of the QC sample ± se
As	29.1 ± 0.9	30.4 ± 1.7* 26.4 ± 0.9	25.8 ± 0.4
Br	770 ± 20	805 ± 6	756 ± 20
Cd	137 ± 2	143.0 ± 2.1	136.7 ± 1.1
Cl	800 ± 25	831 ± 21	796.9 ± 15.6
Cr	100 ± 1.8	99.5 ± 1.0	101.11 ± 0.70
Hg	23.7 ± 0.4	24.43 ± 0.40	22.75 ± 0.44
Pb	98 ± 3	96.0 ± 1.0	100.1 ± 1.3
S	630 ± 20	632 ± 10	645 ± 14
Sb	99 ± 3	99.3± 0.6	93.5 ± 9.1
Sn	86 ± 3	not determined	84.7 ± 4.9
Zn	1250 ± 35	not determined	1258 ± 11

* For As, the results of the two laboratories performing the stability test 2013 are given.

The data of the short-term stability study that demonstrated stability both at elevated temperatures as well as against UV irradiation shows that the stability of ERM-EC681m is as good as the stability of ERM-EC681k. Therefore, the stability of ERM-EC681m can be assessed using the data available for ERM-EC681k.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during dispatch were estimated as described in [19] for each element. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution u_{sts} is calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{tt} \qquad \textbf{Equation 6}$$

RSD relative standard deviation of all results of the stability study

x_i result at time point *i*

$\bar{x}$ mean results for all time points

t_{tt} chosen transport time (1 week at 60 ºC)

Uncertainties of stability during storage were estimated using the long-term stability data available for ERM-EC681k estimated using an approach equivalent to the one for the short-term stability, but adapted to only two time points: The standard uncertainties characterisation study 2006 and of the results of the longest time that confirmed stability (stability test 2013 for As; characterisation study 2015 for all other elements) were combined. This combined uncertainty reflects the uncertainty of stability during the period covered (7 years for As; 9 years for all other elements). The uncertainty of stability for a shelf life of 3 years was therefore estimated as

$$u_{lts,rel} = \frac{\sqrt{u_{1,rel}^2 + u_{2,rel}^2}}{t_{study}} \cdot t_{sl} \qquad \textbf{Equation 7}$$

$u_{1,rel}$, $u_{2,rel}$ uncertainties at the two time points used for the long-term assessment

t_{sl} chosen shelf life (36 months at 18 ºC)

t_{study} time difference between the time-points used for the long-term assessment (7 years for As; 9 years for all other elements)

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies. The uncertainty describes the possible change during a dispatch at 60 °C lasting for one week.

- $u_{lts,rel}$, the stability during storage. This uncertainty contribution was estimated from the data obtained on ERM-EC681k. The uncertainty contribution describes the possible degradation during 3 years (or 36 months) storage at 18 °C.

The results of these evaluations are summarised in Table 6.

Table 6: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 3 years

Element	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
As	0.36	1.66
Br	0.16	1.21
Cd	0.25	0.56
Cl	1.18	1.23
Cr	0.35	0.64
Hg	0.53	0.84
Pb	0.16	1.11
S	1.21	1.30
Sb	0.20	3.23
Sn	0.26	2.21
Zn	0.17	0.98

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to assess its further stability. Special emphasis will be put on As, for which there is indication of a change over time.

6 Characterisation

The material characterisation is the process of determining the assigned property values of a reference material.

The material characterisation was based on an interlaboratory comparison of expert laboratories, i.e. the element mass fractions of the material were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

Twelve laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices as demonstrated by good performance in past characterisation studies organised by JRC-IRMM. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory Where the scope of accreditation covers the measurements, the accreditation number is stated in the list of participants (Section 0).

6.2 Study setup

Laboratories could apply more than one method for each element, resulting in several datasets for these laboratories. For each dataset, each laboratory received two bottles of ERM-EC681m and was requested to provide six independent results, three per bottle.

The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if necessary) and measurements had to be spread over at least two days to ensure intermediate precision conditions. An independent calibration was performed for each result.

Each participant received samples of ERM-EC681k as a quality control material (QCM). The results for this sample were used to support the evaluation of the characterisation results. This material contains Cr and Sn species that are not acid digestible, which means the results on these materials are not suitable for checking laboratory bias for these elements. As mentioned above, the average of As also differed from the certified value. Deviations for As for all methods are therefore expected and were not used for assessment of a method bias.

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 Methods used

A variety of digestion methods (different equipment, different acid mixtures, pressure/temperature programs; combustion in oxygen) with different quantification steps (ICP-QMS, ICP-SFMS, ICP-AES, ETAAS, CV-AAS, CV-AFS, combustion-IC, combustion-IR) as well as a method that does not need digestion (k_0NAA) were used. The combination of results from methods based on entirely different principles mitigates undetected method bias.

All methods used during the characterisation study are summarised in Annex C. The laboratory-method code consists of a number assigned to each laboratory (e.g. L01), a letter (in case the laboratory provided more than one dataset) and abbreviation of the measurement method used, (e.g. ICP-AES). The laboratory number (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 0.

6.4 Evaluation of results

The characterisation campaign resulted in 7-18 datasets per element. All individual results of the participants, grouped per element are displayed in tabular and graphical form in Annex D. Several datasets coming from the same laboratory were treated as independent, even if in some cases the same digestion technique was used. The fact that the digestion technique is often the same does not significantly compromise the independence of results – the potential digestion techniques are limited and no significant laboratory bias was visible for these data.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested measurement protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the measurement protocol: sample preparations and measurements performed on two days; each result for each element obtained from a separate sample preparation;
- the absence of values given as below limit of detection or below limit of quantification;
- method performance, i.e. agreement of the measurement results with the assigned value of the QC sample.

During the investigation of data, the following technical issues were noticed:

L1a: Results obtained by ICP-QMS on the QCM are consistently 10-20 % below the certified values. The laboratory used by far the shortest digestion procedure of all laboratories (7 min). However, the results for ICP-AES (L1b), which agree with the certified values, show that this short procedure does not necessarily result in incomplete digestion of the material/pigments. However, the consistent low findings by ICP-MS indicates a technical bias and the values from ICP-MS were therefore not used for value assignment. Furthermore, the laboratory used pure nitric acid without addition of HF or HCl, which leads to losses for Hg, and maybe also for Sb and Sn due to formation of hydrolysis products.
L1b: The laboratory reported uncertainties for Cd that were more than twice as high as the next highest uncertainties. While the results as agreed with the other values, their accuracy was insufficient for characterisation of a CRM and were not used for characterisation.

L2a: The results of laboratory 2 for Pb obtained on the two CRMs used as QCMs (code L2-ETAAS) differed from the certified values, hinting at a method bias. The results were therefore not used for evaluation.
The uncertainty reported for Sb (29 %) was regarded as too high for characterisation of a CRM. The data were not used for characterisation.

L5a: The laboratory reported biased results for Cr in the QCM. It re-checked the certificate of the spike for Cr by reverse-IDMS using two independent calibration solutions (multi II A Spex and Merck VI) and found that the content on the certificate was biased by a factor 1.2 and the results were corrected for this bias. However, as this investigation was performed as a reaction to a disclosure of results, the data were not used for the value assignment.
L5a, c, d: The laboratory stated very high (80 %) uncertainties for Cr for all three methods (ICP-IDMS, ICP-AES, ICP-SFMS). These high uncertainties are due to the high uncertainty of trueness which was obtained by the bias seen from the analysis of ERM-EC680k and ERM-EC681k. This bias is caused by the presence of insoluble pigments in ERM-EC680k and ERM-EC681k. As the candidate material ERM-EC681m does not contain acid insoluble pigments, these uncertainties are therefore overestimated. The results are therefore retained.
L5b: The results for Hg obtained by AFS on the two QCMs differed from the certified values, indicating a method bias. The data were therefore not used for characterisation.

L6b: The uncertainty reported for ICP-SFMS for Sn (32 %) was regarded as too high for characterisation of a CRM and the data were not used for evaluation.
L6c: The laboratory used ICP-MS for the determination of Cl, which in itself is unusual due to the low ionisation yield for this element. The laboratory also stated itself not to have a lot of experience in the determination of Cl. The laboratory reported results for Cl for ERM-681k that differed from the certified value. The data were therefore not used for evaluation.

L7a: The result for Hg on the CRMs used as QCMs obtained by ICP-IDMS differs from the certified values. After replacement some parts, amongst them the detector, the solutions were re-measured and the results for the QCMs agreed with the certified values. However, the results of the new measurements were not used for value assignment as these measurements were performed only after disclosure of the results from the other laboratories.
L7b obtained a very high standard deviation for Cr, which also resulted in a bimodal distribution. The laboratory stated that this standard deviation was significantly worse than normal. The values were therefore excluded from the value assignment.

L8a: The laboratory reported large differences between the results for As on the QCM obtained by ETAAS on day 1 and day 2. Although this difference was not visible in the candidate CRM, the data were not used for characterisation.
The relative standard deviations obtained for Cd by ETAAS on ERM-EC681k as well as the candidate CRM are very high (30 and 46 % respectively). The method is therefore not fit for these concentration level and the data were not used for evaluation.

Data obtained by ETAAS on Cr and Sn and by ICP-QMS for Sb show a large intermediate precision (10 %, 10 % and 17 %). The methods were deemed insufficiently precise for characterisation of a CRM for these elements and the data were not used.

L9: The laboratory used pure HNO_3 without addition of halogens for digestion. losses of Sn and Sb due to the formation of oxydhydrates. The high standard deviations of results on ERM-EC680m for Sn supports this suspicion. The data for Sn and Sb were therefore not used for characterisation, even if they agreed with the certified values.

L12d: The data for the QCM for Hg deviated from the certified value and the values were therefore excluded from the value assignment.

The issues and actions taken are summarised in Table 7.

Table 7: Summary of the technical noteworthy issues and actions taken in response to them

Element	Lab-method code	Description of problem	Action taken
As	L1a-ICP-QMS	Systematic bias for results from ICP-QMS	Data not used for evaluation
	L8a-ETAAS	Large difference between data on QCM for day 1 and day 2.	Data not used for evaluation
Cd	L1a-ICP-QMS	Systematic bias for results from ICP-QMS	Data not used for evaluation
	L1b-ICP-AES	Uncertainties too high for the characterisation of a CRM.	Data not used for evaluation
	L8a-ETAAS	Method insufficiently precise for the characterisation of a CRM	Data not used for evaluation
Cl	L6c-ICP-SFMS	Result for QCM differs from the certified value; little experience with Cl determinations.	Data for ERM-EC681m not used for evaluation
Cr	L1a-ICP-QMS	Systematic bias for results from ICP-QMS	Data not used for evaluation
	L5a-ICP-IDMS	Spike was found biased	Data not used for evaluation
	L5c-ICP-SFMS, L5d-ICP-AES	Uncertainty is very high (80 %), but this is due to inclusion of the bias determined on ERM-EC681k, which contains non-digestible Cr_2O_3	Data retained
	L7b-ID-TIMS	High standard deviation, bimodal distribution	Data not used for evaluation
	L8a-ETAAS	Intermediate precision (10 %) is insufficient for characterisation of a CRM	Data not used for evaluation
Hg	L1a-ICP-QMS	Systematic bias for results from ICP-QMS; pure HNO_3 used for digestion	Data not used for evaluation
	L5b-AFS	Result for QCM differs from certified value	Data not used for evaluation

Element	Lab-method code	Description of problem	Action taken
	L7a-ICP-IDMS	Result for QCM differs from certified value	Data not used for evaluation
	L12d-CVAFS	Result for QCM differs from certified value	Data not used for evaluation
Pb	L1a-ICP-QMS	Systematic bias for results from ICP-QMS; pure HNO_3 used for digestion	Data not used for evaluation
	L2a-ETAAS	Result for QCM differs from certified value	Data not used for evaluation
Sb	L1a-ICP-QMS	Systematic bias for results from ICP-QMS; use of pure HNO_3 for digestion	Data not used for evaluation
	L2a-ETAAS	Uncertainty is too high for the characterisation of a CRM	Data not used for evaluation
	L8b-ICP-QMS	Method insufficiently precise for the characterisation of a CRM	Data not used for evaluation
	L9-ICP-AES	Use of pure HNO_3 for digestion	Data not used for evaluation
Sn	L1a-ICP-QMS	Systematic bias for results from ICP-QMS; ; use of pure HNO_3 for digestion	Data not used for evaluation
	L5d- ICP-AES	Uncertainty is very high (80 %), but this is due to inclusion of the bias determined on ERM-EC681k, which contains non-digestible SnO_2	Data retained
	L6b-ICP-SFMS	Uncertainty is too high for the characterisation of a CRM	Data not used for evaluation
	L8a-ETAAS	Method insufficiently precise for the characterisation of a CRM	Data not used for evaluation
	L9-ICP-AES	Result for the QCMs differed from the certified value; use of pure HNO_3 for digestion	Data not used for evaluation
Zn	L1a-ICP-QMS	Systematic bias for results from ICP-QMS	Data not used for evaluation

6.4.2 Statistical evaluation

The technically datasets were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots. They were also analysed for outlying means using the Grubbs test and for outlying standard deviations using the Cochran test for outlying standard deviations, (both at a 99 % confidence level). Standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 8.

Table 8: Statistical evaluation of the technically accepted datasets for ERM-EC681m. *p*: number of technically valid datasets

Element	*p*	Outliers		Normally distrib.?	Statistical parameters			
		Means	Variances		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
As	14	none	L1b, L9 (retained)	yes	17.00	0.90	0.85	0.75
Br	7	none	none	yes	1434	88	86	42
Cd	16	none	L5c (retained)	yes	146.3	4.4	3.9	5.2
Cl	6	none	L2d (retained)	no	378.0	11.9	9.2	18.6
Cr	15	none	L5c (retained)	yes	45.05	2.17	2.07	1.63
Hg	8	none	none	yes	9.875	0.810	0.795	0.388
Pb	14	none	none	approx..	69.71	3.18	3.00	2.54
S	9	none	L5f (retained)	yes	638.5	37.9	35.1	34.0
Sb	11	L8a	none	no	86.34	4.06	3.86	3.05
Sn	11	none	none	yes	99.19	4.29	3.85	4.63
Zn	17	none	none	yes	1174	51	48	41

The datasets for As, Br, Cd, Cr, Hg, Pb, S, Sn, and Zn do not contain outlying mean values and the data follow normal/approximately normal distributions. The statistical evaluation flagged some data as outliers of variance. This merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value.

The dataset for Cl does not contain any outlying mean, but L2d was flagged as outlier of variance. As the dataset was technically sound, it was retained. The dataset does not follow a normal distribution, with four dataset means between 384 and 386 mg/kg and two more at 357 and 371 mg/kg, respectively. However, all datasets agree with one another within their respective uncertainties and all datasets include the arithmetic mean of laboratory means within their expanded uncertainty. The datasets are therefore consistent and the mean of laboratory means is a sufficiently reliable estimate of the true value.

For Sb, the data obtained by ETAAS by laboratory 8 (L8a) are flagged as an outlier on a 99 % confidence level, which means that the data do not follow a normal distribution. However, it must be borne in mind that outlier tests do not take uncertainty information into consideration. A closer investigation reveals that the difference between the mean value of laboratory 8 and the other results is covered by the measurement uncertainty of laboratory 8. There is therefore no evidence that the results of laboratory by ETAAS deviate from the other results. The datasets are therefore consistent and the mean of laboratory means is a sufficiently reliable estimate of the true value.

It is interesting to see that for Hg, all data from NAA are above all other data. No explanation for this effect can be found: A bias of NAA should be visible also for the other long-lived elements. A bias of all other methods is equally unlikely, as they all agreed with the certified value for ERM-EC680k and during the characterisation of ERM-EC680k, no such bias was observed. As all results agree with the certified value, this effect, if real, is technically insignificant and the unweighted mean of laboratory means is still a valid estimate of the true value.

Table 9: Uncertainty of characterisation for ERM-EC681m

Element	*p*	Mean [mg/kg]	*s* [mg/kg]	$u_{char,rel}$ [%]
As	14	17.00	0.90	1.41
Br	7	1434	88	2.32
Cd	16	146.3	4.4	0.75
Cl	6	378.0	11.9	1.29
Cr	15	45.05	2.17	1.24
Hg	8	9.875	0.810	2.90
Pb	14	69.71	3.18	1.22
S	9	638.5	37.9	1.98
Sb	11	86.34	4.06	1.42
Sn	11	99.19	4.29	1.30
Zn	17	1174	51	1.05

7 Value Assignment

Certified values were assigned. Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3] were established.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 8 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 0), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (Section 5). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,\,rel}$) with a coverage factor *k* as:

$$U_{CRM,rel} = k \cdot \sqrt{u^2_{char,rel} + u^2_{bb,rel} + u^2_{sts,rel} + u^2_{lts,rel}} \qquad \textbf{Equation 8}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1.
- u_{sts} was estimated as described in section 5.3
- u_{lts} was estimated as described in Section 5.3.

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor *k* of 2 was applied, to obtain the expanded uncertainties.

The certified values and their uncertainties are summarised in Table 10.

Table 10: Certified values and their uncertainties for ERM-EC681m

Element	Certified value [mg/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [1)]
As	17.0	1.41	2.41	0.36	1.66	6.54	1.2
Br	$1.43 \cdot 10^3$	2.32	0.49	0.16	1.21	5.33	$0.08 \cdot 10^3$
Cd	146	0.75	1.12	0.25	0.56	2.96	5
Cl	$0.38 \cdot 10^3$	1.29	6.77	1.18	1.23	14.20	$0.06 \cdot 10^3$
Cr	45.1	1.24	1.49	0.35	0.64	4.15	1.9
Hg	9.9	2.90	2.14	0.53	0.84	7.48	0.8
Pb	69.7	1.22	0.59	0.16	1.11	3.51	2.5
S	$0.64 \cdot 10^3$	1.98	6.97	1.21	1.30	14.92	$0.10 \cdot 10^3$
Sb	86	1.42	0.69	0.20	3.23	7.20	7
Sn	99	1.30	0.73	0.26	2.21	5.36	6
Zn	$1.17 \cdot 10^3$	1.05	0.53	0.17	0.98	3.09	$0.04 \cdot 10^3$

[1)] Expanded (k = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

All elements are chemically clearly defined substances. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The measurand is therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. Different calibrants of specified traceability of their assigned values were used and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as it is also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific (or specific groups) of analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CLSI Guideline C-53A [20] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

ERM-EC681m was produced from commercial polymers and commercially available pigments. The analytical behaviour will be the same as for a routine sample of coloured polyethylene. For samples other than polyethylene the commutability has to be assessed.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials shall be stored at (18 ± 5) °C in the dark. The user is reminded to close bottles immediately after taking a sample.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.3 Minimum sample intake

The minimum sample intake representative for all parameters is 150 mg for Cl and 60 mg for all other elements.

9.4 Use of the certified value

The main purpose of this material is to assess method performance, i.e. for checking accuracy of analytical results/calibration. Note that if the tested material contains insoluble pigments, results obtained on this CRM may not be representative for the tested sample for wet digestion methods.
As any reference material, it can also be used for control charts or validation studies or for calibration.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [21].

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty ($u_{\Delta,}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %

- If $\Delta_{meas} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as inhomogeneity was included in the uncertainties of the certified values.

Use as a calibrant

It is not recommended to use this matrix material as calibrant, because the certified values have higher uncertainties than pure standards. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

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Annexes

Annex A: Results of the homogeneity measurements

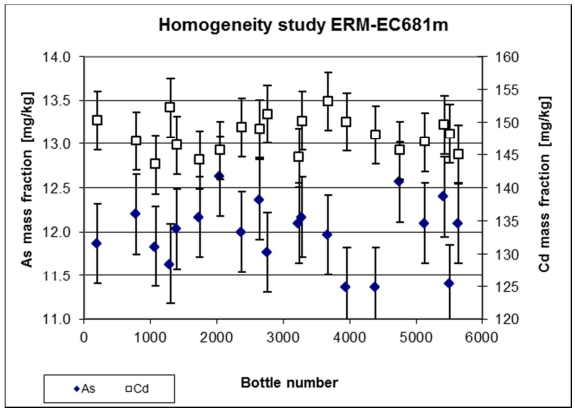
Annex B: Results of the short-term stability measurements

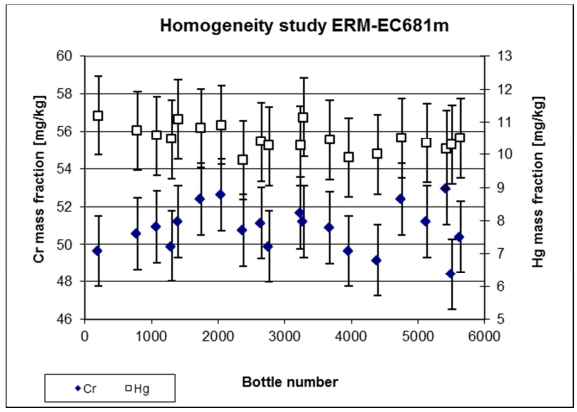
Annex C: Summary of methods used in the characterisation study

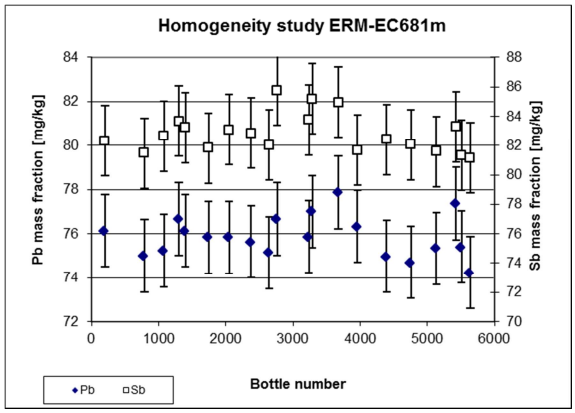
Annex D: Results of the characterisation measurements

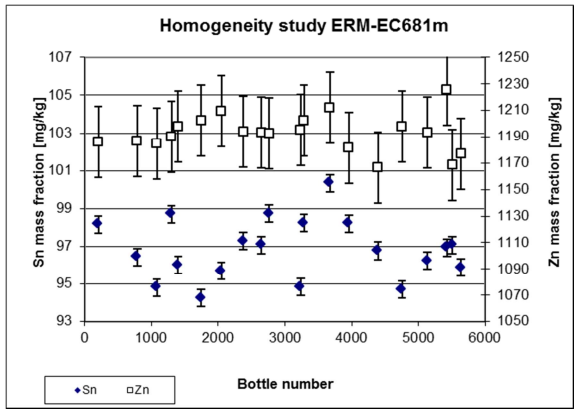
Annex A: **Results of the homogeneity study**. Shown are the bottle means and their confidence intervals (95 %; n=3), based on the within-bottle standard deviation as derived by ANOVA.

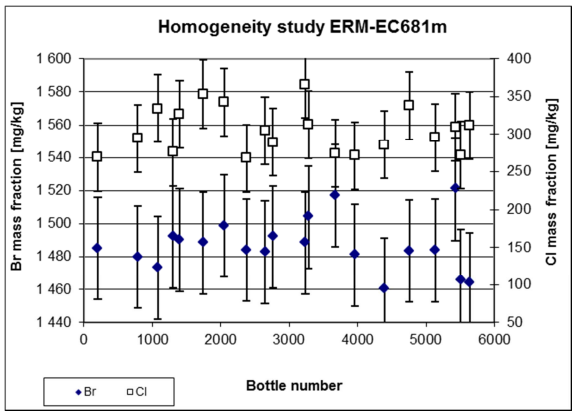
Note that the results were obtained by one laboratory only and in some cases differ from the certified value. Although the absolute values of several elements differ from the certified values, this should influence the homogeneity assessment, which compares only results within the measurement series.

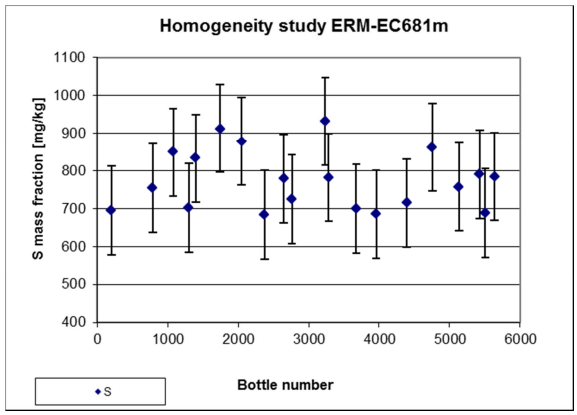






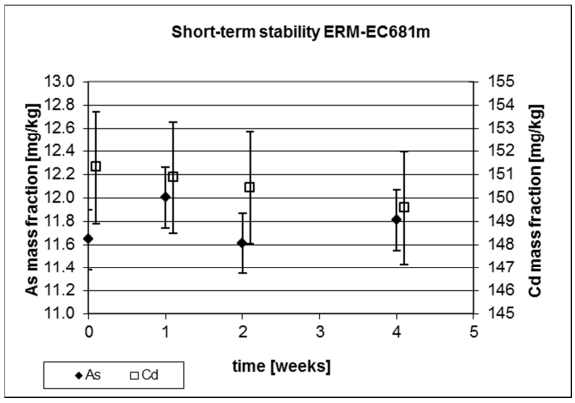


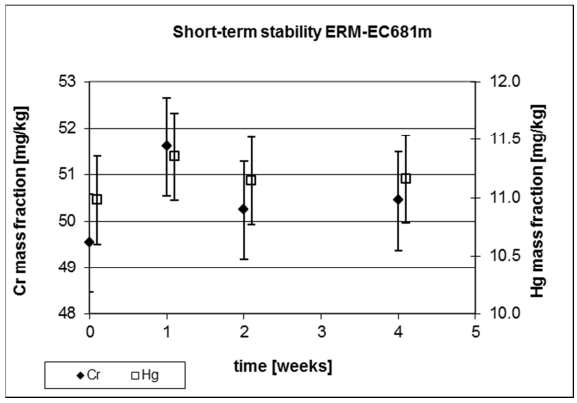


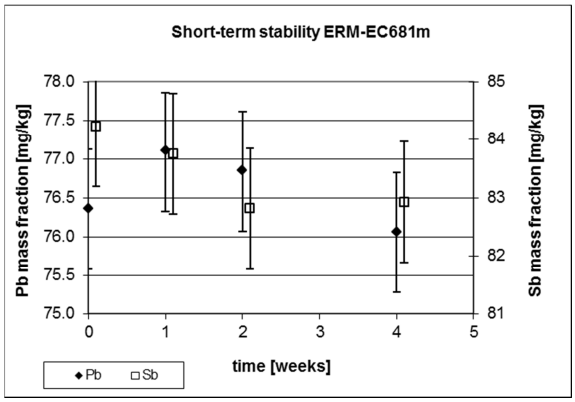


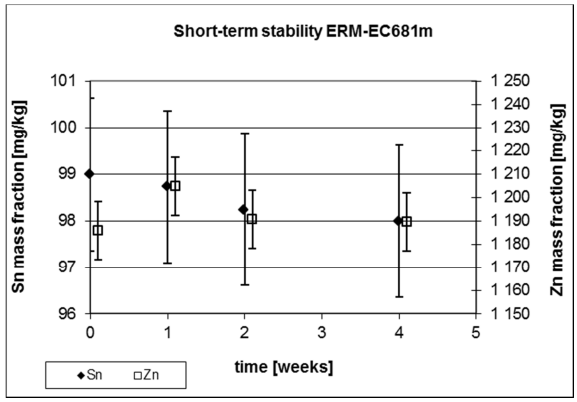
Annex B: **Results of the short-term stability study at 60 °C**. Shown are the averages per time point and their confidence interval (95 %; n=15) based on the within-group standard deviation as derived from an one-way ANOVA of all data grouped by time. The time points were 0, 1, 2 and 4 weeks for both elements in each graph, but the data were separated graphically to facilitate reading.

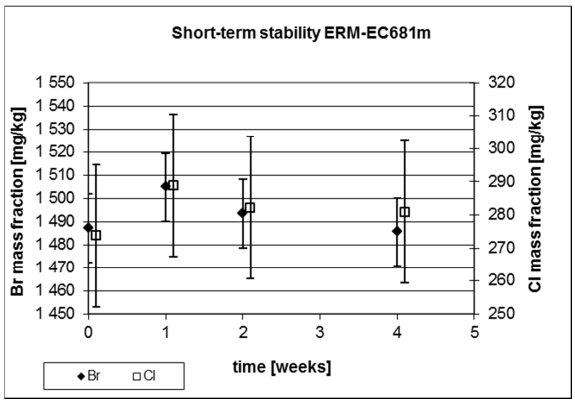
Note that the results were obtained by one laboratory only and in some cases differ from the certified value. Although the absolute values of several elements differ from the certified values, this should influence the homogeneity assessment, which compares only results within the measurement series.

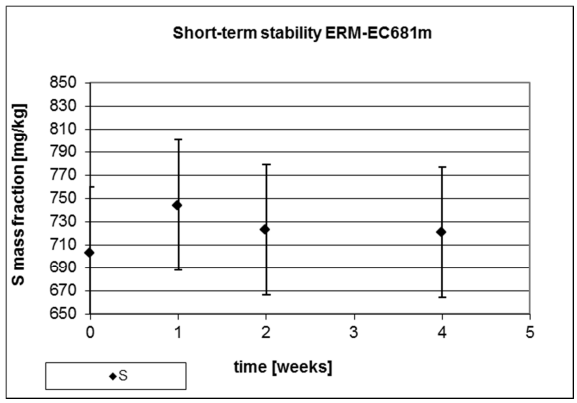












Annex C: Summary of methods used in the characterisation study.

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L1a	ICP-QMS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	200-300 mg	Closed microwave digestion using CEM Discover SP-D Explorer 24 Plus 10 mL HNO_3; 200 °C, 300 bar, 7 min Dilution to 50 mL and additional dilution 1:10	Multielement standard Romil; traceability ensured by a CRM; Internal standard: Y	ICP-MS on mass 75 (As), 111 (Cd), 52 (Cr), 202 (Hg), 208 (Pb), 121 (Sb), 118 (Sn), 66 (Zn)
L1b	ICP-AES	As, Cd, Cr, Pb, Sb	200-220 mg	Closed microwave digestion using CEM Discover SP-D Explorer 24 Plus 10 mL HNO_3; 200 °C, 300 bar, 7 min Dilution to 50 mL	Multielement standard Romil; traceability ensured by a CRM	ICP-AES on 189.042 nm (As), 228.802 nm (Cd) 267.716 nm (Cr), 220.353 nm (Pb), 182.034 nm (Sb), 206200 nm (Zn)
L2a	ETAAS CV-AAS	Cd, Pb, Sb Hg	300-500 mg	Closed microwave digestion: 1 mL HNO3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed	ETAAS according to CEN/TS 16172 (Cd, Pb, Sb) on 228.8 nm (Cd), 283.3 nm (Pb), 217.6 nm (Sb) CV-AAS according to EN ISO 12846 with reductant NaBH4 (Hg) on 253.7 nm (Hg)
L2b	ICP-QMS	As, Br, Cr, Sn, Ge, Zn	300-500 mg	Closed microwave digestion: 1 mL HNO_3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed Internal standard: Rh (As, Br), Ge (Cr, Zn), In (Sn)	ICP-MS according to EN ISO 17294-2 on mass 75 (As), 79 and 81 (Br), 52 (Cr), 118 and 120 (Sn), 68 (Zn)

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L2c	ICP-AES	S	300-500 mg	Closed microwave digestion: 1 mL HNO_3/1 mL HCl/1 mL HF for 300 mg sample; 240 °C, 60 bar, 1 h Complexation of free fluoride by addition of 11 ml H_3BO_4 (4 %, s.p.)	Commercial standards from Alfa-Aesar, Merck, Maker Instra Analyzed	ICP-OES according to EN ISO 11885 on 180.669 nm (S)
L2d	Combustion-IC	Cl	500 mg	IKA - Kalorimetersystem C 2000 basic IKA – Kalorimeterbombe C 5012 O_2, 30 bar, 30 min 10 mL aqueous absorption solution (Na_2CO_3, $NaHCO_3$, NaOH, H_2O_2)	Commercial standards	IC according to EN ISO 10304-1 (Cl)
L3	k_0NAA	As, Cd, Cr, Hg, Sb, Sn, Zn	170-200 mg	Irradiation for 1170 min at $7.4 \cdot 10^{12}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 3-6 d;	HPGe P-type, 25 % rel efficiency; measurement time 1 h
		Br, Cl,	170-200 mg	Irradiation for 1 min at $2 \cdot 10^{13}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 8 and 45 min	HPGe P-type, 25% rel efficiency; measurement time 15 and 20 min
L4	k_0NAA	As, Br, Cd, Sn	550 -700 mg	Irradiation for 15 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 2-5 d;	HPGe detector, 40 – 55 % rel efficiency; measurement time 24-48 h
		Cr, Hg, Sb, Zn		Irradiation for 420 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 15-25 d;	HPGe detector, 40 – 55 % rel efficiency; measurement time 24-48 h
		Cl		Irradiation for 15 min at $3 \cdot 10^{11}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 (Al-Au); decay time 30-900 s	HPGe detector, 40 – 55 % rel efficiency; measurement time 900 s

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L5a	ICP-IDMS	Cd, Cr, Pb, Zn	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Spike solution Certipur ^{111}Cd, ^{206}Pb, (Merck), enriched ^{53}Cr(VI) Applied isotope technologies), ^{68}Zn (Spex Certiprep)	Sectorfield ICP-MS on masses 11/112 (low resolution; Cd), 52/53 (medium resolution; Cr), 206/208 (low resolution; Pb), 66/68 (high resolution; Zn)
L5b	AFS	Hg	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Merck standard checked against NIST SRM 3133	AFS at 253.7 nm
L5c	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	150 mg	High Pressure asher 4 mL HNO_3/1 mL HCL at 200 °C and up to 200 bar; 210 min	Standards from CPI international checked against NIST SRM 3100 series (As, Cd, Cr, Pb, Sn, Zn) and NIST SRM 3102a (Sb) Internal standard Rh	ICP-AES at 189.042 nm (As), 214.438 nm (Cd), 205.552 nm (Cr), 220.353 nm (Pb), 206.833 nm (Sb), 189.989 nm (Sn), 213.856 nm (Zn)
L5d	ICP-SFMS	As, Cd, Cr, Pb, Sb, Sn, Zn	150 mg	High Pressure asher 4 mL HNO_3 + 1 mL HCL at 200 °C and up to 200 bar; 210 min	Mono- and multielement standards from SPEX checked against NIST SRM 3103a (As, Cd, Cr, Pb, Zn), NIST SRM 3102a (Sb), NST SRM 3161a (Sn); internal standard Ge (As), Rh (all others)	Sectorfield ICP-MS on masses 75 (As; high resolution), 114 (Cd), 52 (Cr), 206, 207, 208 (Pb), 121 (Sb), 118 (Sn) and 66 (Zn) (all medium resolution)
L5e	Combustion/IC	Br, Cl, S	530-600 mg	Parr 6200 calorimeter 30 bar O_2, 5 mL (0.1 M NaOH solution + 3 mL H_2O_2 / L 0.1 M NaOH) in bomb and 10 mL in absorption flask	Merck standards checked against NIST NaBr in water/NaCl in water/Na2SO4 in water	IC (of 3.2 mM Na2CO3/ and 1.0 mM NaHCO3) with conductivity and UV detection in combination with conductivity suppression

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L5f	Combustion-IR	S	100-160 mg	LECO Truspec S at 3 bar aqnd 1350 C samples weighed in a dry combustion boat and covered with about 1.5 g baked white sand; combustion at 1350 °C in oxygen	LECO 502-55 (Orchard leaves), 0.148 % S	LECO Truspec S
L6a	ICP-IDMS	Cd, Cr, Hg, Pb, Zn	100-110 mg	Milestone Ultraclave at 230 °C/90 bar; 40 min ramping time, 25 min hold at 230 °C 5 ml HNO_3 / 0.020 ml HF	Isotope dilution MS characterization using enriched isotopes from Oak Ridge National Laboratory	ICP-MS on masses 111, 112, 114 (Cd), 52, 53 (Cr), 199, 200, 202 (Hg), 206, 208 (Pb), 64, 66, 67 (Zn)
L6b	ICP-SFMS	As, Cd, Cr, Hg, Pb, S, Ab, Sn, Zn	150-200 mg	Milestone Ultraclave at 230 °C for 20 min in HNO_3/HF	Standards from Inorganic Venture (Zn) and Ultra Scientific (all others); traceability via NIST 3103a (As), NIST 3108 (Cd), NIST 3112a (Cr), NIST 3133 (Hg), NIST 3128 (Pb), NIST 3154 (S), NIST 3102a (Sb), NIST 3161a (Sn), NIST 3168a (Zn) Internal standard: In	Quantification by ICP-SFMS in high resolution at mass 75 (As), medium resolution at mass 52, 53 (Cr), 32 (S), 64, 66 (Zn) and low resolution at mass 111, 114 (Cd), 201, 202 (Hg), 206, 207, 208 (Pb), 121, 123 (Sb), 118, 120 (Sn)
L6c	ICP-SFMS	Br, Cl	150-200 mg	Microwave digestion at 220 °C for 30 min in HNO_3	Standards from Ultra Scientific (Br) and Fluka (Cl); traceability via NIST 3184 (Br) and SA71387	Quantification by ICP-SFMS in medium resolution at mass 79 (Br), 35 (Cl)
L7a	ID-TIMS (Cd, Pb) ICP-IDMS (Hg)	Cd, Pb, Hg	210-240 mg	High Pressure Asher at 320 °C/130 bar for 240 min in 4.5 mL HNO_3/0.5 mL H_2O_2 Separation of the analytes by column chromatography	Double IDMS with ^{113}Cd, ^{201}Hg, ^{206}Pb, ^{207}Pb isotopic spikes from the Bundesanstalt fuer Materiaforschung und -Pruefung	Cd, Pb: Quantification by TIMS at mass 110, 111, 112, 113 and 114 (Cd) and 204, 206, 207, 208 (Pb) using a mass resolution of 400 Hg: Quantification by ICPMS at mass 201, 202 and a mass resolution of 400

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L7b	ID-TIMS	Cr	400-420 mg	Ashing in a microwave-heated muffle oven with subsequent soda fusion melting of the ash. Separation of the analytes by column chromatography	Double IDMS with ^{53}Cr from the Bundesanstalt fuer Materiaforschung und -Pruefung	Quantification by TIMS at mass 52, 53 using a mass resolution of 400
L8a	ETAAS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	200 mg	Milestone Ultraclave at 250 °C/140 bar for 30-60 min 4 mL HNO_3 + 0.2 mL $HClO_4$	Standards from ChemLal; traceability via NIST 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3133 (Hg), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NIST SRM 3168a (Zn)	ETAAS with background correction at 193.7 nm (As), 228.8 nm (Cd), 357.9 nm (Cr), 253.7 nm (Hg), 283.3 nm (Pb), 217.6 nm (Sb), 286.3 nm (Sn), 307.6 nm (Zn)
L8b	ICP-QMS	As, Cd, Cr, Hg, Pb, Sb, Sn, Zn	170-180 mg	Milestone Ultraclave at 250 °C/135 bar for 45 min 4.0 mL HNO_3 + 0.1 mL HCl	Standards from inorganic Ventures with traceability via NIST SRM 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3133 (Hg), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NISt SRM 3168a (Zn) Internal standard In (mass 115)	ICP-MS at masses 75 (As), 111 (Cd), 52 (Cr), 202 (Hg), 206, 207, 208 (Pb), 121 (Sb), 118 (Sn), 66 (Zn) Mass resolution 70-280
L8c	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	200-210 mg	Milestone Ultraclave at 250 °C/140 bar for 60 min 4.0 mL HNO_3 + 0.2 mL $HClO_4$	Standards from Chemlab with traceability via NIST SRM 3103a (As), NIST SRM 3108 (Cd), NIST SRM 3112a (Cr), NIST SRM 3128 (Pb), NIST SRM 3102a (Sb), NIST SRM 3161a (Sn), NISt SRM 3168a (Zn) Internal standard Sc	ICP-AES at 188.979 nm (As), 214.438 nm (Cd), 205.56 nm (Cr), 220.353 nm (Pb), 206.836 nm (Sb), 198.933 nm (Sn), 213.856 nm (Zn)

Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L9	ICP-AES	As, Cd, Cr, Pb, Sb, Sn, Zn	200-220 mg	Microwave digestion (Milestone ETHOS 900) at 140-220 °C for 60 min 8 mL HNO_3 65%	Monoelement standards from Carlo Arba (As, Sn) multielement standards from Sigma (Cd, Cr, Pb, Sb, Zn) with traceability via NIST SRM 3103a (As), NIST SRM 728 (Cd, Pb, Zn), NIST SRM 2112 (Cr), NIST SRM 3102a (Sb)	ICP-AES at 188.979 nm (As), 226.502 nm (Cd), 267.716 nm (Cr), 220.353 nm (Pb), 206.836 nm (Sb), 189.927 nm (Sn), 206.200 nm (Zn)
L10	k0NAA	Cr, Hg, Sb, Sn, Zn As, Br, Cd, Cl	160-170 mg	Irradiation for 720 min at $1.10^{\cdot}10^{12}$ neutrons/cm2/s Irradiation for 5 min at $2^{\cdot}10^{13}$ neutrons/cm^2/s	Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 19-30 d; Kayzero-evaluation using IRMM-530 R (Al-Au); decay time 4 d (As, Br), 7-9 d (Cd), 20 min (Cl)	HPGe P-type, 40-45 % rel efficiency; measurement time 9-17 h HPGe P-type, 25% rel efficiency; measurement time 100 min (As, Br), 20 min (Cl), 9-16 h (Cd)
L11	ICP-AES	As, Cd, Cr, Pb, S, Sb, Sn, Zn	500 mg	Milestone Ultraclave at 240 °C/105 bar for 240 min 4.0 mL HNO_3 + 0.5 mL HF +0.2 mL H_2O_2	Single-element standards from Merck; traceable via NISt SRMs	ICP-AES at 189 nm & 197 nm (control) (As), 228 nm & 226 nm (control) (Cd), 267 nm & 284 nm (control) (Cr), 220 nm & 216 nm (control) (Pb), 180 nm & 182 nm (control) (S), 206 nm & 217 nm (control)(Sb), 189 nm (Sn), 213 nm & 202 nm (control) (Zn)
L12a	ICP-MS	As, Cd, Cr, Pb, S, Sb, Sn, Zn	220-250 mg	Bomb digestion (Berghof) at 220 °C/60 min 5 mL HNO_3 + 2.5 mL H_2O_2 + 0.4 mL HF (according to NEN-EN-ISO 16968)	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs	ICP-MS with collision cell technology at masses 75 (As), 111 (Cd), 52 (Cr), 201 (Hg), 208, 207, 206 (Pb), 34 (S), 121 (Sb), 118 (Sn), 66 (Zn)

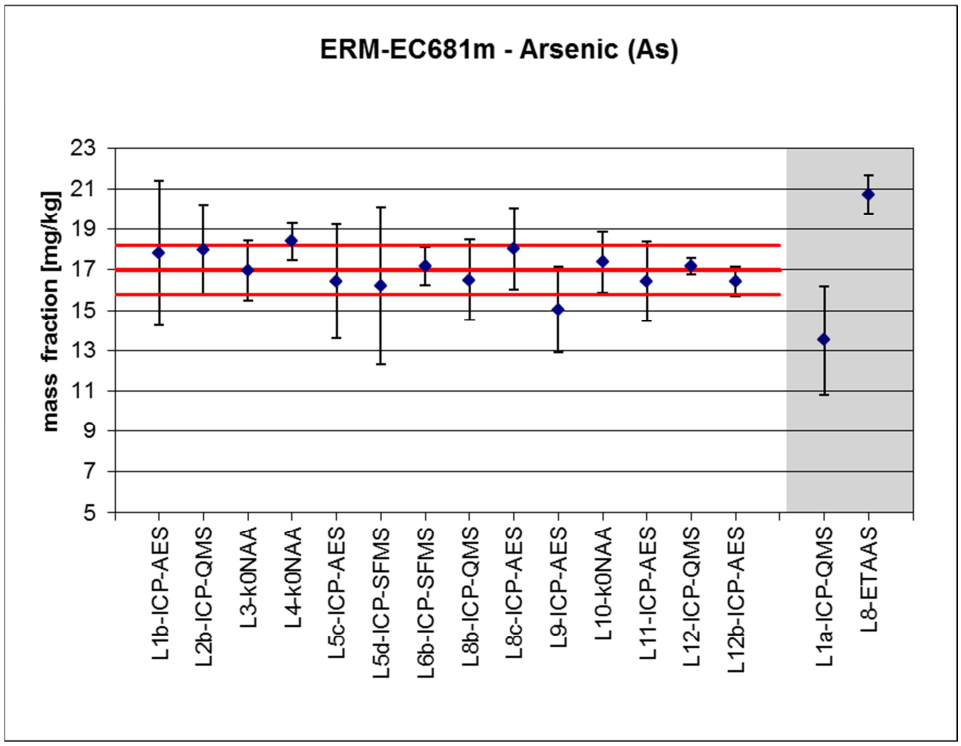
Data-set	Method	Elements	Sample mass [mg]	Sample preparation	Calibration	Instrumentation and measurement method
L12b	ICP-AES	As, Cd, Cr, Pb, S, Sb, Sn, Zn	250 mg	Bomb digestion (Berghof) at 190 °C/600 min 9.5g HNO_3 + 4.5 g $HClO_4$; After digestion dilution to 50 g and addition of 0.5 mL HF	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs Internal standard Sc	ICP-AES at 193.7 nm (As), 214.4 nm (Cd), 267.7 nm (Cr), 220.3 nm (Pb), 182 nm (S), 217.5 nm (Sb), 189.9 nm (Sn), 206.2 nm (Zn)
L12c	Combusion-IC	Br, Cl, S	500-700	Digestion in 30 bar oxygen (bomb calorimeter PARR 6300); bomb is rinsed with 100 mL water	Stock solutions from crystalline NaBr, NaCl and Na2SO4 (suprapur, Merck KgA, DE), checked against NIST-CRM	Ion chromatography on a Dionex IonPac AS18 (4 x 250mm) column. Gradient elution with an Eluent Generator Cartridge (KOH).
L12d	CV-AFS	Hg	250 mg	Bomb digestion (Berghof) at 190 °C/600 min 5 mL HNO_3 + 2.5 mL $HCLO_4$; After digestion dilution to 50 g and addition of 0.5 mL HF (digestion together with 12b)	Custom-made standards by Inorganic Ventures; traceability via NIST SRMs Internal standard Sc	CV-AFS at 254 nm

Annex D: Results of the characterisation measurements. Given are the results reported by the laboratories and the uncertainties reported for the average of 6 results (For averages marked with an asterisk, no uncertainty was given. In these cases, two times the standard deviation was entered as uncertainty).

The solid red lines in the graph show the certified value and the upper and lower limit of the certified range (95 % uncertainty). Laboratories not used for value assignment are separated in the graphs by the space in these red lines.

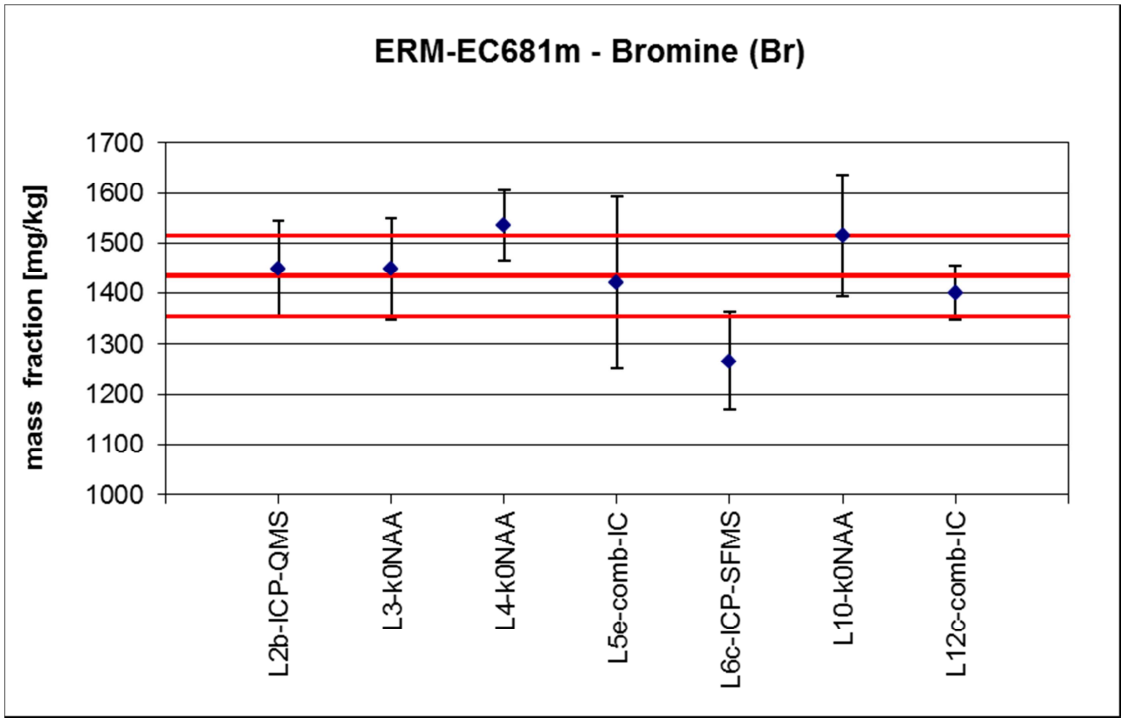
As-Arsenic(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L1b-ICP-AES	21	18	16	18	16.9	17	17.8	20
L2b-ICP-QMS	17	19	19	18	17	18	18.0	12.2
L3-k0NAA	17.4	16.4	17.1	17.1	16.8	16.9	17.0	8.8
L4-k0NAA	18.1	18.2	18.3	18.7	18.4	18.8	18.4	5.0
L5c-ICP-AES	16.0	15.6	16.0	15.9	17.9	17.2	16.4	17.1
L5d-ICP-SFMS	15.7	16.9	16.1	16.0	16.9	15.6	16.2	24.1
L6b-ICP-SFMS	17.3	16.5	17.6	17.5	17.5	16.7	17.2	5.5
L8b-ICP-QMS	16	16	17	16	17	17	16.5	12.1
L8c-ICP-AES	17.5	17.9	18.4	17.8	18.6	18.0	18.0	11.1
L9-ICP-AES	16.7	16.3	13.5	14.7	14.3	14.7	15.0	14.0
L10-k0NAA	17.9	17.9	17.3	17.3	16.9	17	17.4	8.6
L11-ICP-AES	16.5	16.3	16.3	17.1	16.4	16	16.4	12*
L12a-ICP-QMS	17.44	17.19	17.22	17.06	17.43	16.83	17.2	2.4
L12b-ICP-AES	16.33	16.17	16.87	15.99	16.9	16.37	16.4	4.5
Data not used for certification								
L1a-ICP-QMS	14.8	14.4	13.7	13.6	13	11.5	13.5	20
L8-ETAAS	20.3	20.9	21.1	21.4	20.4	20.3	20.7	4.6*



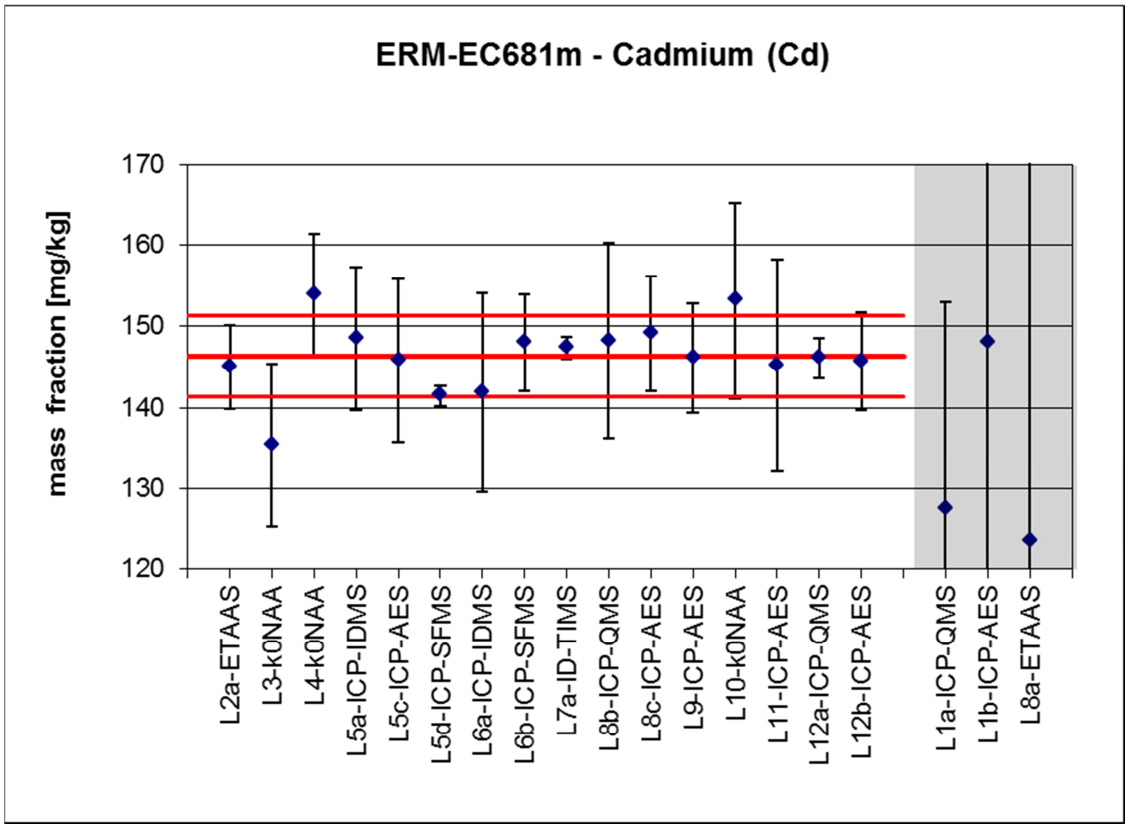
Br-Bromine

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2b-ICP-QMS	1400	1500	1500	1400	1400	1500	1450	6.5
L3-k0NAA	1450	1448	1435	1406	1472	1485	1449	6.9
L4-k0NAA	1538	1522	1526	1545	1489	1593	1535	4.6
L5e-comb-IC	1473	1431	1458	1447	1410	1312	1422	12.0
L6c-ICP-SFMS	1280	1330	1190	1300	1260	1240	1267	7.7
L10-k0NAA	1553	1528	1489	1481	1532	1505	1515	7.9
L12c-comb-IC	1423	1359	1396	1398	1395	1438	1402	3.8



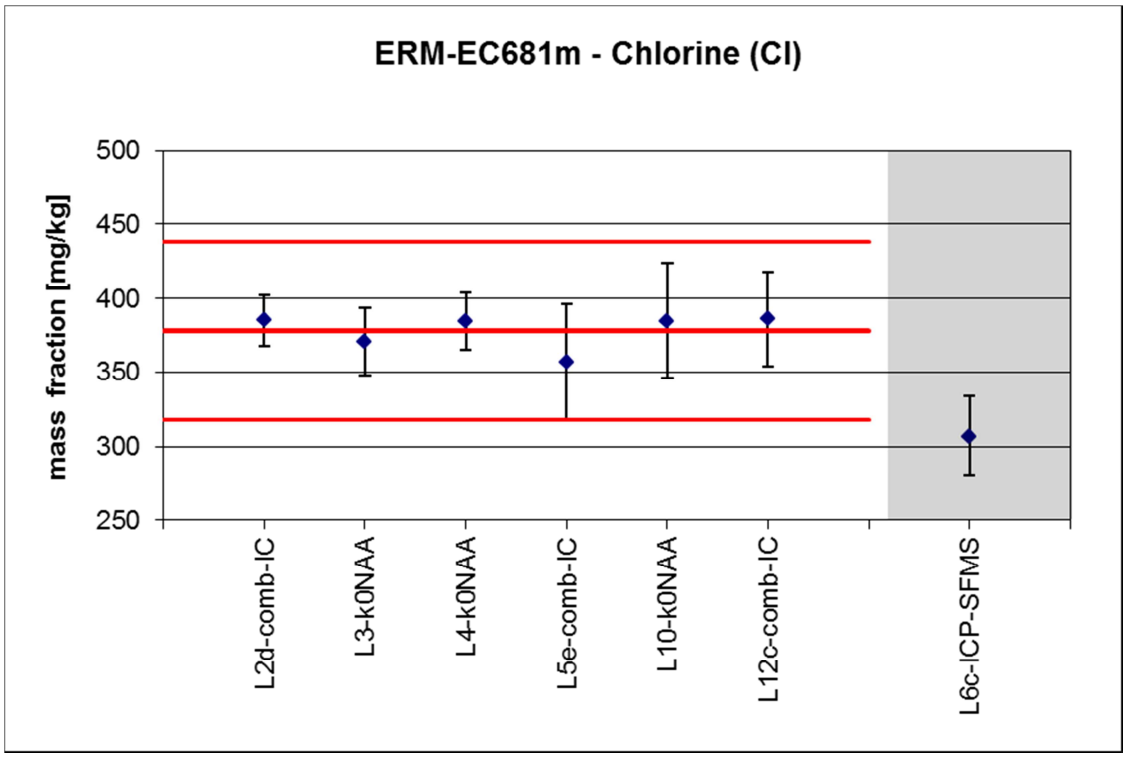
Cd-Cadmium(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-ETAAS	150	140	140	160	140	140	145.0	3.5
L3-k0NAA	142	136	130	140	134	130	135.3	7.4
L4-k0NAA	153.9	152.2	151.3	154.5	149.0	162.2	153.9	4.85
L5a-ICP-IDMS	159.7	143.6	140.6	150.1	145.2	151.3	148.4	5.9
L5c-ICP-AES	141.8	139.1	138.0	156.5	138.0	161.6	145.8	6.9
L5d-ICP-SFMS	140.2	147.0	137.5	141.5	142.9	139.7	141.5	0.92
L6a-ICP-IDMS	148	141	149	136	134	143	141.8	8.67
L6b-ICP-SFMS	149	149	148	152	147	143	148.0	4.01
L7a-ID-TIMS	149.95	149.05	143.86	147.49	146.97	146.68	147.3	0.9
L8b-ICP-QMS	144.2	148.6	150.7	146.3	149.9	149.4	148.2	8.1
L8c-ICP-AES	142.2	148.6	151.7	147	155.8	149.2	149.1	4.7
L9-ICP-AES	135	141	149	148	152	152	146.2	4.58
L10-k0NAA	156	152	152	150	155	154	153.2	7.83
L11-ICP-AES	144	150	143	146	146	142	145.2	9
L12a-ICP-QMS	146.4	144.6	144.6	147.1	149.9	144	146.1	1.7
L12b-ICP-AES	145.7	144.7	144.7	151.5	144.5	143	145.7	4.1
Data not used for certification								
L1a-ICP-QMS	138	136.7	132.1	128.8	120.8	108.8	127.5	20
L1b-ICP-AES	140.5	142.5	157.4	151.7	145.9	149.6	147.9	20
L8a-ETAAS	88.48	193.631	186.698	83.932	82.3	105.711	123.5	84.8*



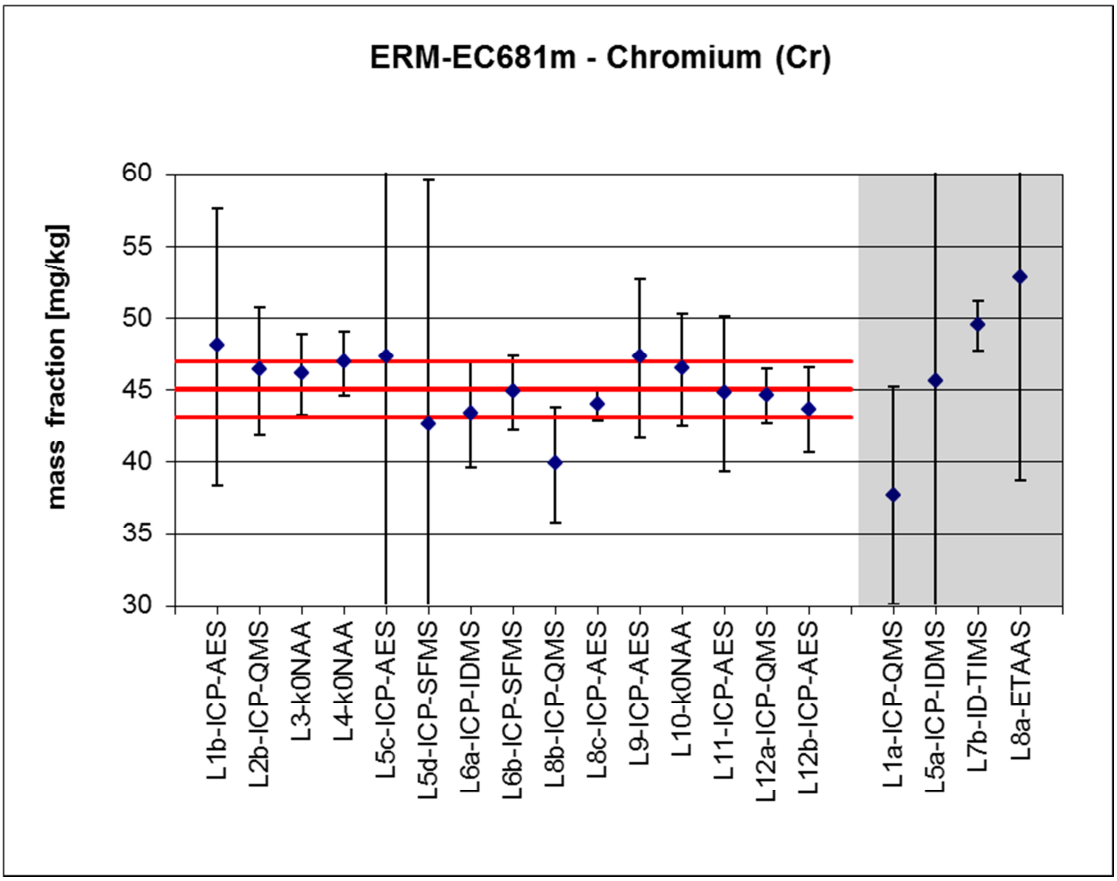
Cl-Chlorine(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2d-comb-IC	380	360	410	410	330	420	385.0	4.4
L3-k0NAA	381	364	364	365	370	378	370.3	6.2
L4-k0NAA	400	384	386	377	385	378	384.9	5.1
L5e-comb-IC	376	368	369	346	349	333	356.8	11.0
L10-k0NAA	368	386	403	379	374	399	384.8	10.1
L12c-comb-IC	371	379.2	372.2	412.1	383	397.5	385.8	8.4
Data not used for certification								
L6c-ICP-SFMS	299	328	291	317	305	302	307.0	8.7



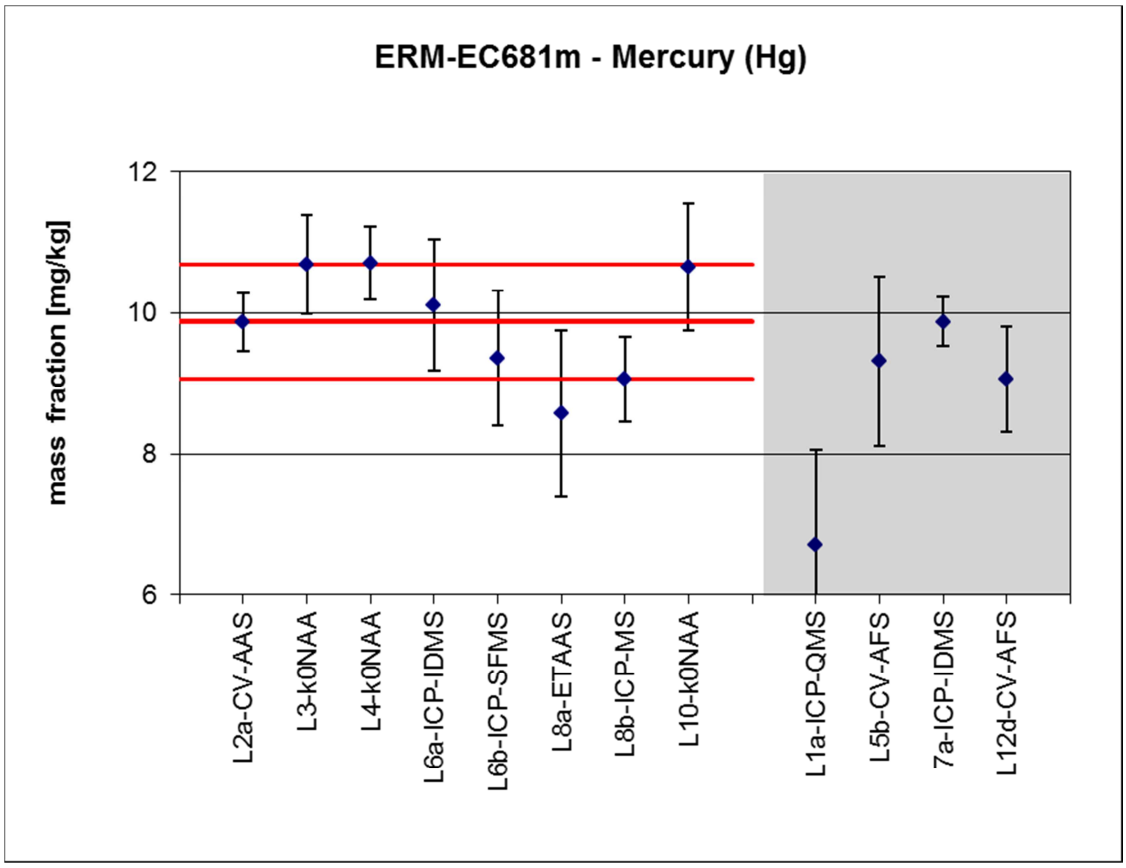
Cr-Chromium (results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L1b-ICP-AES	50.3	47	49.2	47.6	47	47	48.0	20.0
L2b-ICP-QMS	47	47	47	46	45	46	46.3	9.5
L3-k0NAA	47	45.7	45.1	47.7	46.5	44.7	46.1	6.1
L4-k0NAA	47.1	45.5	45.8	48.5	46.2	48.1	46.9	4.8
L5c-ICP-AES	45.1	43.7	43.8	49.9	52.2	48.6	47.2	82.6
L5d-ICP-SFMS	42.4	42.9	41.4	42.6	43.6	42.7	42.6	39.9
L6a-ICP-IDMS	45.5	43.3	41	45.3	41.5	43.5	43.4	8.5
L6b-ICP-SFMS	44.3	43	44.7	46.8	45.5	44.7	44.8	5.7
L8b-ICP-QMS	37	39	41	40	42	40	39.8	10.1
L8c-ICP-AES	42.88	44.6	44.83	42.8	44.98	43.66	44.0	2.3
L9-ICP-AES	42.9	45.2	48.7	47.7	49.6	49.4	47.3	11.6
L10-k0NAA	48.1	46.1	45.1	45.8	47.4	46.1	46.4	8.4
L11-ICP-AES	44.7	45.9	44	45.6	44.8	43.5	44.8	12.0*
L12a-ICP-QMS	45.64	44.93	45.19	44.23	44.6	43.08	44.6	4.2
L12b-ICP-AES	43.76	43.43	45.11	41.02	44.95	43.51	43.6	6.7
Data not used for certification								
L1a-ICP-QMS	41	39.9	39.9	38.2	34.7	32.3	37.7	20.0
L5a-ICP-IDMS	46.4	45.5	44.0	46.2	45.0	46.2	45.6	45.9
L7b-ID-TIMS	45.4	46.0	53.8	45.8	51.0	54.6	49.4	3.5
L8a-ETAAS	58.6	53.6	62.5	48.2	43.3	50.2	52.7	26.6*



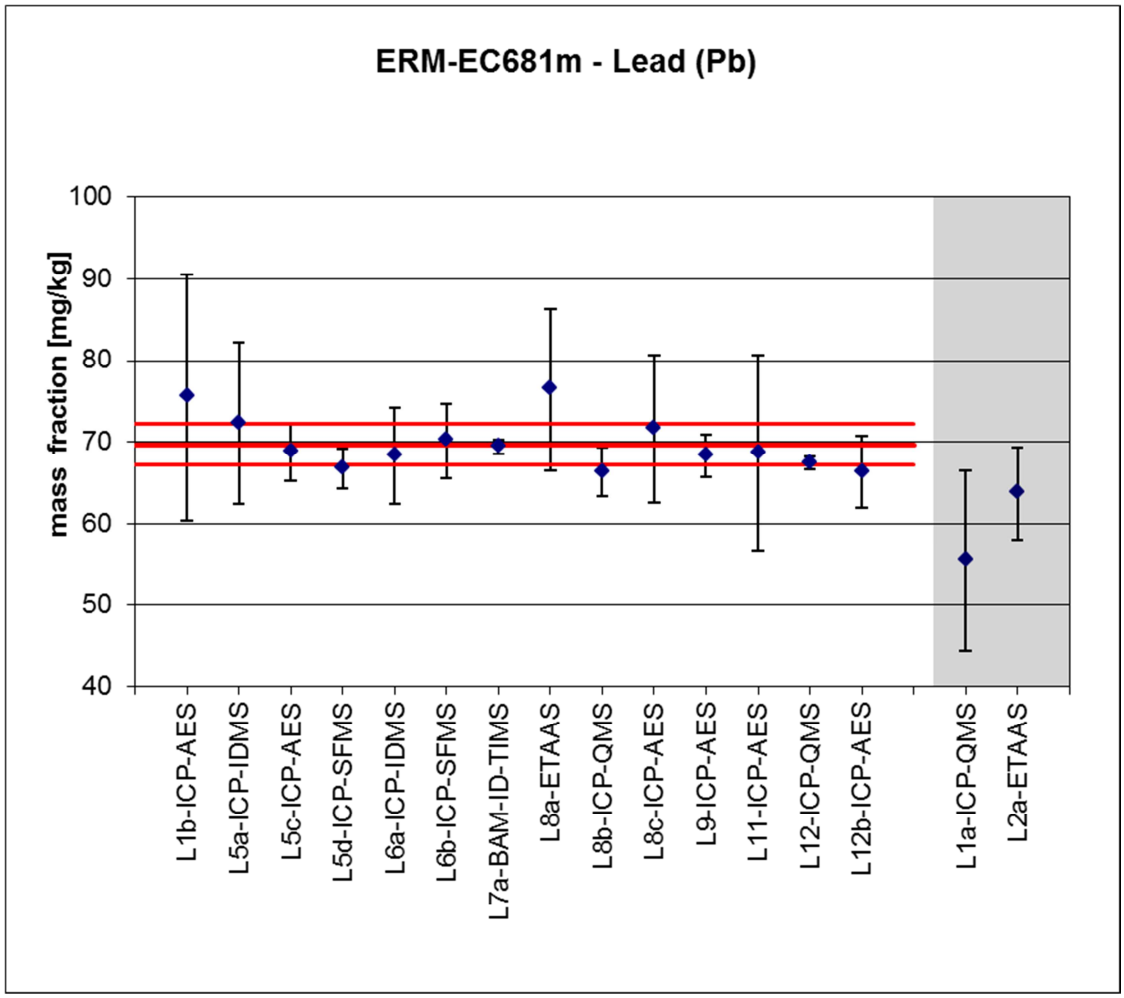
Hg-Mercury (results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2a-CV-AAS	9.6	10	10.5	9.8	9.6	9.7	9.87	4.1
L3-k0NAA	10.9	10.5	10.4	11	10.9	10.4	10.68	6.6
L4-k0NAA	10.8	10.4	10.5	11.0	10.5	10.9	10.70	4.8
L6a-ICP-IDMS	9.67	10.3	10.8	9.69	9.79	10.4	10.11	9.1
L6b-ICP-SFMS	8.73	9.33	8.96	10	9.75	9.38	9.36	10.1
L8a-ETAAS	8.52	9.30	9.19	8.11	8.54	7.78	8.57	13.8*
L8b-ICP-QMS	8.7	8.8	9.3	9.3	8.9	9.4	9.07	6.6
L10-k0NAA	11.1	10.6	10.4	10.4	10.8	10.6	10.65	8.5
Data not used for certification								
L1a-ICP-QMS	6.6	6.5	6.7	6.8	7	6.7	6.72	20.0
L5b-CV-AFS	9.31	9.61	8.8	9.1	9.43	9.68	9.32	12.8
L7a-ICP-IDMS	9.90	9.96	10.03	9.71	9.71	9.91	9.87	3.5
L12d-CV-AFS	9.2	8.8	9.6	8.8	9.3	8.6	9.06	8.2



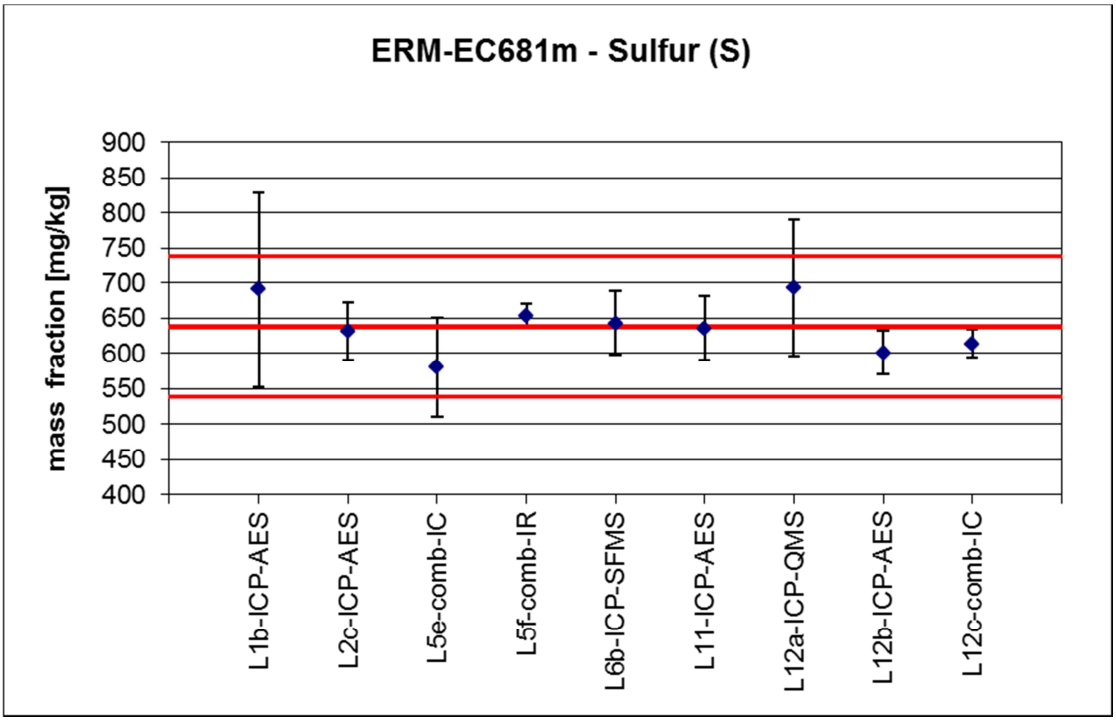
Pb-Lead (results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L1b-ICP-AES	78.1	75.1	78.2	76.3	73	72.1	75.5	20
L5a-ICP-IDMS	74.7	72.0	70.6	73.1	70.4	72.6	72.2	13.7
L5c-ICP-AES	68.1	63.7	64.3	73.3	73.3	70.1	68.8	5.1
L5d-ICP-SFMS	66.3	69.2	64.6	67.2	67.5	65.8	66.8	3.7
L6a-ICP-IDMS	71.6	68.4	71.3	65	64.7	68.5	68.3	8.64
L6b-ICP-SFMS	67	70.5	73.3	71.8	69.8	68.4	70.1	6.49
L7a-ID-TIMS	68.04	70.51	69.16	68.31	70.2	70.13	69.4	1.2
L8a-ETAAS	73.7	69.5	73.5	78.6	81.4	81.8	76.4	12.9*
L8b-ICP-QMS	64	67	68	67	66	66	66.3	4.52
L8c-ICP-AES	69	71.58	73.32	70.43	74.11	71.05	71.6	12.6
L9-ICP-AES	64.1	66.3	68.4	68.4	71.2	71.1	68.3	3.81
L11-ICP-AES	68	71	67	70	69	67	68.7	17.5
L12a-ICP-QMS	67.9	67.0	67.1	67.1	68.7	66.7	67.4	1.2
L12b-ICP-AES	66.2	67.4	68.4	62.3	67.6	65.9	66.3	6.6
Data not used for certification								
L1a-ICP-QMS	60.2	59	58.5	55.4	51.4	47.6	55.4	20
L2a-ETAAS	62	58	78	62	61	61	63.7	8.9



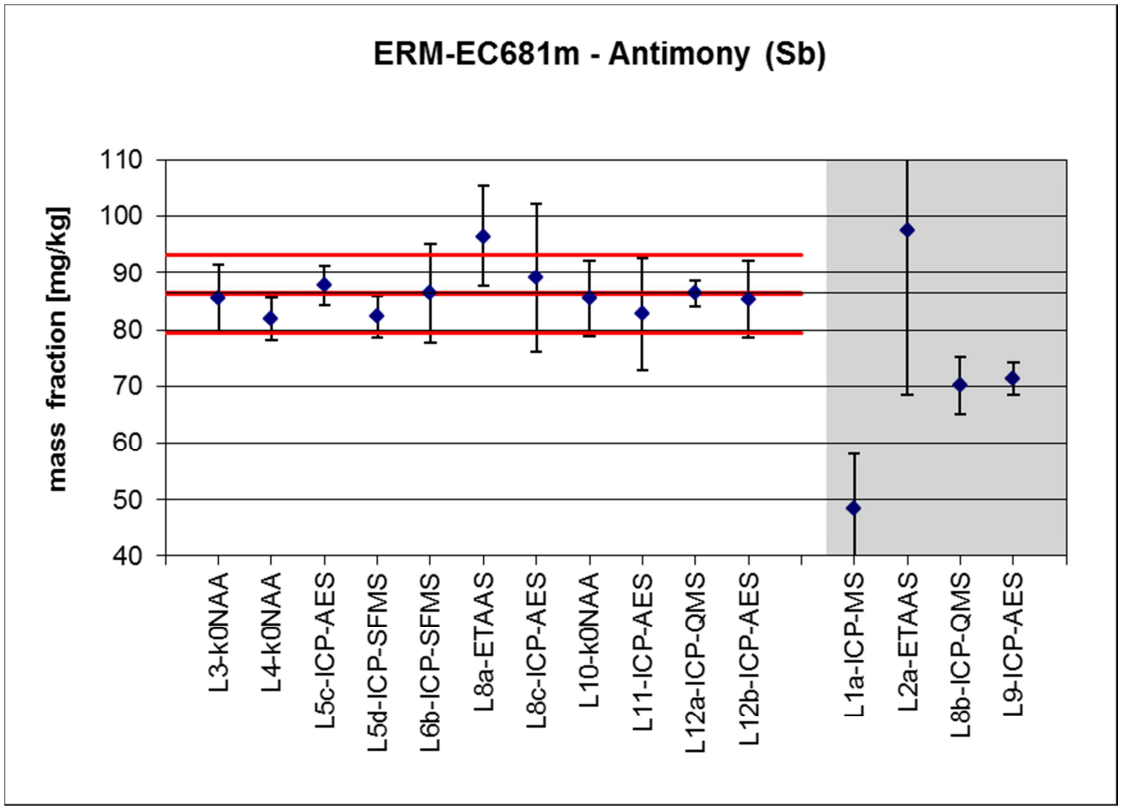
S-Sulfur

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L1b-ICP-AES	703.7	664.3	700.1	737.4	685.3	655.2	691.0	20.0
L2c-ICP-AES	630	620	650	620	620	650	631.7	6.5
L5e-comb-IC	646	590	583	562	558	548	581.2	12.0
L5f-comb-IR	795	660	647	614	582	628	654.3	2.4
L6b-ICP-SFMS	599	637	656	657	658	652	643.2	7.2
L11-ICP-AES	626	645	617	647	654	627	636.0	7.2
L12a-ICP-QMS	632.8	734.9	657.3	699.9	687.2	754	694.4	14
L12b-ICP-AES	594.2	610.4	611.3	577.4	619.8	594.1	601.2	5.1
L12c-comb-IC	623.3	613.9	601.1	606.7	615.1	623.5	613.9	3.3



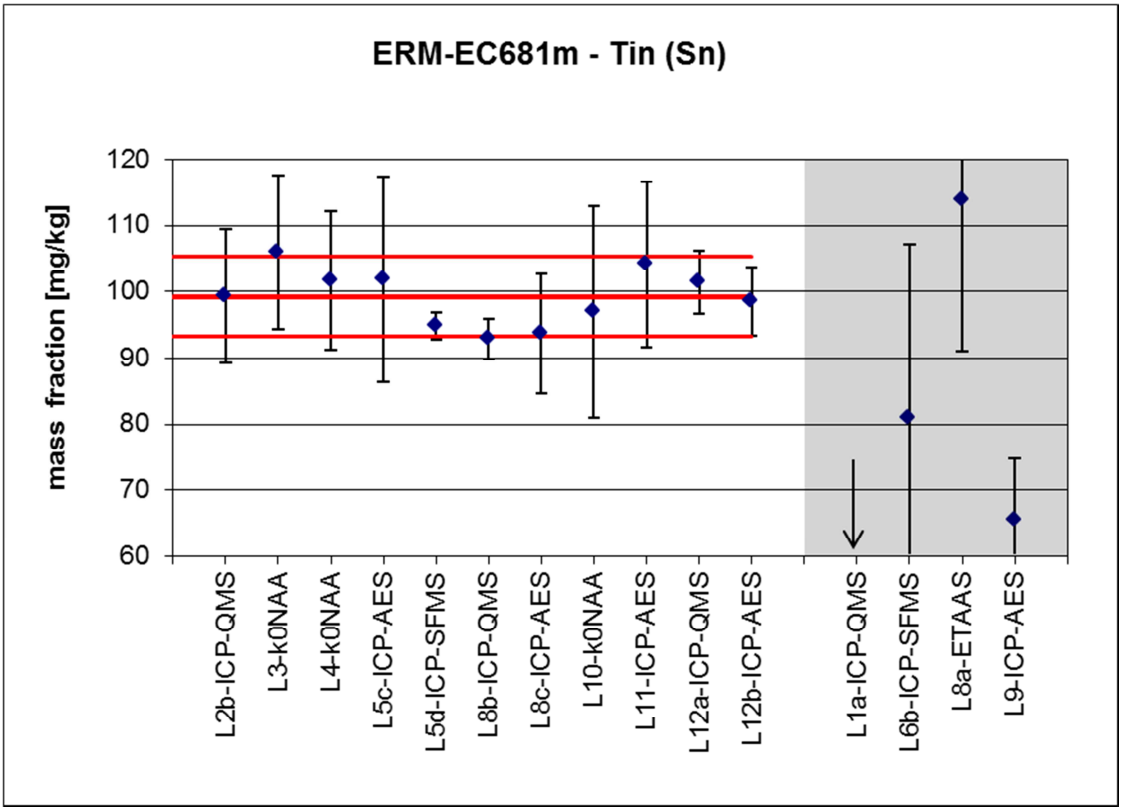
Sb-Antimony(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L3-k0NAA	87.3	84.6	83.5	88.2	86.8	83	85.6	7.1
L4-k0NAA	82.1	80.4	81.0	83.3	79.9	85.0	81.9	4.6
L5c-ICP-AES	84.8	84.1	81.1	91.3	95.9	90.0	87.9	4.0
L5d-ICP-SFMS	80.7	85.0	79.8	82.4	85.0	80.7	82.3	4.4
L6b-ICP-SFMS	82.4	82.6	85.4	93.1	90.3	84.5	86.4	10.1
L8a-ETAAS	98.0	101.1	98.9	88.4	96.5	96.1	96.5	9.1*
L8c-ICP-AES	87.2	88.5	91.4	89.2	91.1	87.8	89.2	14.6
L10-k0NAA	87.5	86	84.5	83.4	86.5	85	85.5	7.8
L11-ICP-AES	81.6	84.6	80.8	84.1	83.4	82.1	82.8	12*
L12a-ICP-QMS	87.8	85.1	86.0	86.4	88.1	84.7	86.3	2.5
L12b-ICP-AES	83.9	84.8	91.3	81.7	86.9	83.6	85.4	7.9
Data not used for certification								
L1a-ICP-QMS	43.3	46.5	44.8	54.9	52.8		48.5	20.0
L2a-ETAAS	100	100	100	96	96	93	97.5	29.7
L8b-ICP-QMS	53	59	69	81	82	77	70.2	7.1
L9-ICP-AES	68.6	69.2	73.5	76	72.4	68.4	71.4	3.9



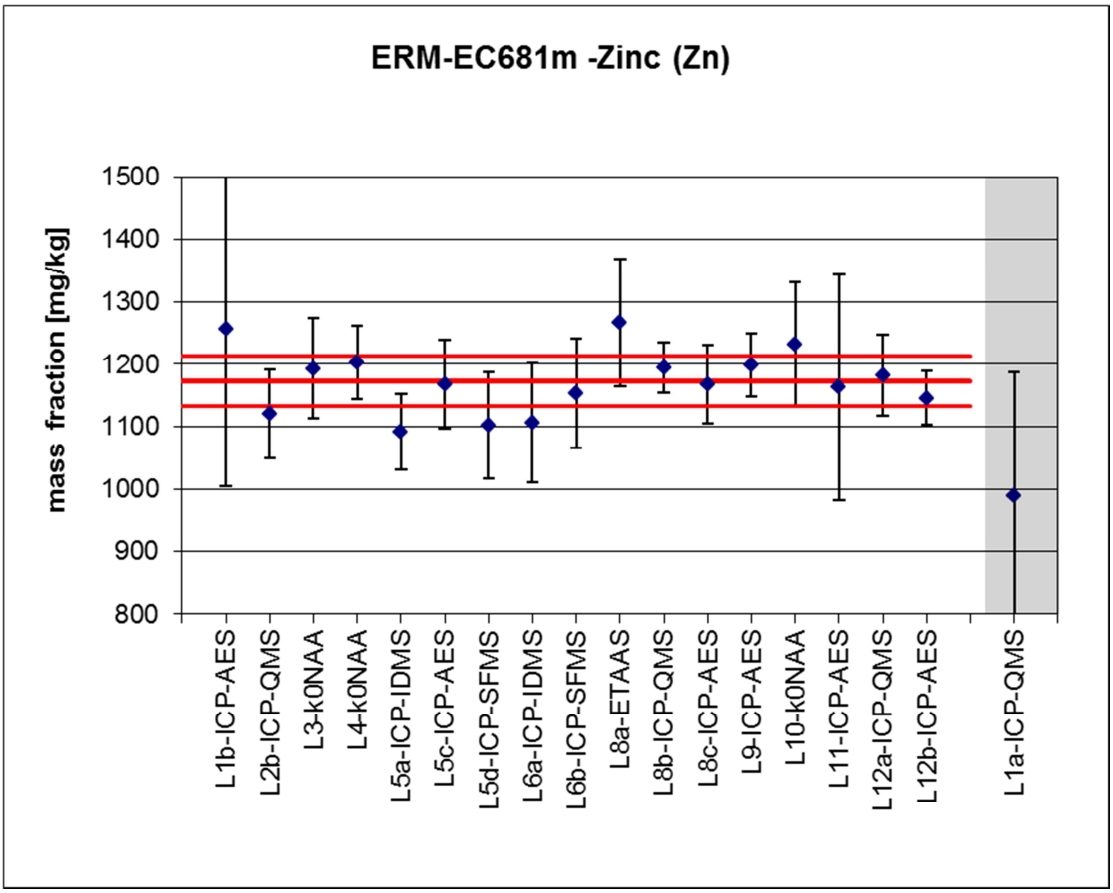
Sn-Tin(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L2b-ICP-QMS	99	99	100	100	98	100	99.3	10.1
L3-k0NAA	105	108	110	108	105	100	106.0	11.0
L4-k0NAA	102	101	101	107	95	103	101.6	10.3
L5c-ICP-AES	96	94	95	106	113	108	101.9	15.2*
L5d-ICP-SFMS	94	97	93	94	98	93	94.8	2.1
L8b-ICP-QMS	82	86	92	102	100	95	92.8	3.2
L8c-ICP-AES	92.6	93.0	96.2	96.5	94.4	89.6	93.7	9.6
L10-k0NAA	95.7	96.2	103	100	103	83.8	97.0	16.4
L11-ICP-AES	105.8	110	104.1	103.2	102.6	99.4	104.2	12.0
L12a-ICP-QMS	103.6	102.0	102.9	99.7	101.9	98.1	101.4	4.7
L12b-ICP-AES	96.0	96.8	98.2	102.9	99.7	96.9	98.4	5.2
Data not used for certification								
L1a-ICP-QMS	20.4	27.4	25.8	14	13.2	18.3	19.9	20.0
L6b-ICP-SFMS	68.6	95.3	64.8	85.7	94.9	76	80.9	32.4
L8a-ETAAS	105	104	103	126	128	117	113.8	20.0*
L9-ICP-AES	65.3	59.8	73.8	77.5	61.6	54.1	65.4	14.4



Zn-Zinc(results in the grey shaded part of the graph were not used for value assignment)

Laboratory code	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [%]
L1b-ICP-AES	1 227	1 238	1 325	1 274	1 257	1 220	1256.9	20.0
L2b-ICP-QMS	1 120	1 123	1 176	1 095	1 084	1 131	1121.5	6.3
L3-k0NAA	1 213	1 186	1 169	1 228	1 206	1 155	1192.8	6.7
L4-k0NAA	1 216	1 184	1 202	1 220	1 184	1 216	1203.8	4.9
L5a-ICP-IDMS	1 224	1 027	1 021	1 087	1 109	1 086	1092.4	5.5
L5c-ICP-AES	1 108	1 108	1 094	1 223	1 276	1 197	1167.8	6.1
L5d-ICP-SFMS	1 066	1 095	1 082	1 135	1 152	1 086	1102.4	7.7
L6a-ICP-IDMS	1 160	1 110	1 160	1 060	1 050	1 100	1106.7	8.6
L6b-ICP-SFMS	1 110	1 140	1 200	1 200	1 170	1 100	1153.3	7.6
L8a-ETAAS	1 329	1 292	1 231	1 248	1 195	1 306	1266.8	8.0*
L8b-ICP-QMS	1 175	1 179	1 213	1 192	1 194	1 215	1194.7	3.4
L8c-ICP-AES	1 111	1 167	1 182	1 159	1 213	1 175	1167.8	5.4
L9-ICP-AES	1 100	1 150	1 230	1 230	1 240	1 240	1198.3	4.2
L10-k0NAA	1 263	1 248	1 226	1 197	1 239	1 222	1232.5	8.0
L11-ICP-AES	1 150	1 190	1 140	1 180	1 170	1 150	1163.3	15.5
L12a-ICP-QMS	1 199	1 197	1 212	1 153	1 195	1 137	1182.2	5.5
L12b-ICP-AES	1 148	1 141	1 140	1 188	1 134	1 127	1146.3	3.8
Data not used for certification								
L1a-ICP-QMS	1 067	1 069	1 026	1 004	924	853	990.4	20.0



European Commission

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